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PHYSICAL APPLICATIONS OF THE LORENTZ GROUP*

By B. S. Madhava Rao

1. Introduction

As is well known, the Lorentz group entered physics through the setting up of Einstein's special theory of relativity, and since this theory is crucial for many a physical theory, the Lorentz group plays a fundamental role in physics. This is especially true in the field of elementary particles where the relativity and quantum theory are brought into close fusion. While the very concept of elementary particles is quantum-mechanical in origin, it is certainly true that relativity, and hence the notion of Lorentz invariance have been crucial for the development of quantum theory.

We can define the general Lorentz transformation as a linear co-ordinate transformation connecting two inertial frames x^i and $x^{i'}$ $(i, i' = 1, 2, 3, 4)$, *viz.*,

$$x^{i'} = a^i + \lambda_j^i x^j \quad (i, j = 1, 2, 3, 4) \tag{1}$$

which leaves the Minkowskian quadratic differential form

$$ds^2 = (dx^4)^2 - (dx^1)^2 - (dx^2)^2 - (dx^3)^2 \quad (x^4 = ct) \tag{2}$$

invariant. It need hardly be said that the importance of this transformation is a result of the postulate of special relativity that, in the absence of gravitation, the laws of physics have the same form in all inertial frames of reference, that any two such frames are connected by a transformation specified by (1) and (2), and that c is an invariant in this transformation. It is easily seen that the set of these transformations constitutes a group, and this is called the general Lorentz group, and the essential requirement of special relativity may thus be stated as the invariance of any physical theory under the group of Lorentz transformations. It may happen, however, that for a satisfactory explanation of the theory not all Lorentz transformations of the general type need necessarily be admitted. The minimal requirement so far has been that the theory be invariant with respect to the restricted Lorentz group (denoted here by L_4) consisting of all transformations

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for which $\lambda_4{}^4 > 0$, and the determinant of the $\lambda_j{}^i$, *viz.*, $|\lambda_j{}^i| = 1$; in other words, the subgroup not including the transformations of space reflections and time reversal. These latter types can be classified under the three headings:—

$$(a)\ x^{i'} = -x^i\ (i = 1, 2, 3),\ x^{4'} = x^4 \tag{3}$$

being the space reflections denoted by P; this letter is used so as to correspond to the notion of parity which is $\pm$, according as the wave function associated with a particle does not or does change sign under space reflections alone;

$$(b)\ x^{i'} = x^i\ (i = 1, 2, 3),\ x^{4'} = -x^4 \tag{4}$$

being the time reversal denoted by T; and

$$(c)\ x^{i'} = -x^i\ (i = 1, 2, 3, 4) \tag{5}$$

being the total inversion which is the product of P and T.

It is evident that the set of elements of P or T do not constitute subgroups of the general group, and moreover these sets are not of any physical interest by themselves alone since invariance under L_4 is a minimal requirement. We therefore consider the elements PL_4, TL_4, and PTL_4, and build the subgroups (L_4, PL_4), (L_4, TL_4), and (L_4, TPL_4) each containing L_4 as a proper subgroup of itself. In the earlier years of the theory of elementary particles, where free particles were in the centre of interest, invariance under L_4 played a prominent part, but in recent years the centre of interest has shifted to interactions between several types of particles, and it is found that the other three types of subgroups mentioned above have also to be taken into consideration.

2. Relativistic Quantum Theory

Confining oneself for the moment to a theory invariant under L_4 we might mention two striking examples of its early successes. Starting from the notion of a photon, the relation $E = cp$ (including $E = mc^2$) between the energy and momentum of a particle is a relativistic one. The other example is the de Broglie relation $p = h/\lambda$, which follows from Planck's relation $E = h\nu$ on the basis of invariance under L_4. It is however with the introduction of Dirac's equation of the electron inaugurating relativistic quantum mechanics, and the subsequent work of Pauli establishing the connection between spin and statistics on the basis of this theory that the full importance of the Lorentz group in physical applications was clearly brought out, by emphasising the role of the irreducible representations of L_4. In

particular, the notion of spin of an elementary particle could be made precise on the basis of such representations.

The relativistic quantum theory consists essentially of two stages in its application, the *c*-number theory with the wave functions and field equations for the particles satisfying the postulates of relativity, and the *q*-number theory making a transition to the particle picture by using the quantum conditions expressing the non-commutation of the field functions at different points of space-time. Such a passage from the *c*-number to the *q*-number theory is called double quantisation.

The essential steps in the *c*-number theory are the setting up of a Lagrangian invariant for transformations of the proper Lorentz group, *i.e.*, the continuous Lorentz group $\mathbf{L}_4$ in which no reflections are included, the derivation of the field equations from a variational principle, the setting up of the energy-momentum and angular momentum tensors, and lastly dividing the field quantities into $\mathrm{U}(x)$, their conjugates $\mathrm{U}^*(x)$, and the real quantities $\mathrm{V}(x)$ and assuming the invariance of the Lagrangian under gauge transformations. Since the field equations are derived from a Lagrangian, the field quantities themselves should transform according to irreducible representations of the group $\mathbf{L}_4$. Such quantities are, as is well known, the spinors, and the field quantity can be written as $\mathrm{U}(j, k)$ characterised by two indices j and k corresponding to spinors with $2j$ undotted, and $2k$ dotted indices, and symmetric in them. Using the Clebsch-Gordon rule for the reduction of product representations, and the situation in the case of the subgroup of space rotations, one defines the spin of the particle as $j + k$. For the case $2j + 2k =$ even, the spinors reduce to the ordinary world tensors, but not for the case $2j + 2k =$ odd. Working with these general field quantities, we find the general results that for particles of half-integral spin, the total energy is not necessarily positive, and for integral spin the charge density is not necessarily positive. Going to the *q*-number theory and using the fact that the expressions for the non-commutation of the field quantities at different points should themselves satisfy invariance relations, these relations can be written in terms of the bracket expressions:

$$[\mathrm{U}(x),\ \mathrm{U}^*(x')]^{\pm} = \mathrm{D}(x, x') \qquad (6)$$

the $+$ or $-$ being taken according as the particles satisfy the Fermi-Dirac (F.D.) or Einstein-Bose (E.B.) statistics, where further the transformation properties of the U's under L also require that the D's should transform in a certain way. By merely considering the algebraic nature of the transformations of the D's under $\mathbf{L}_4$, with the further requirements that D is a

function of the invariant distance between x and x', and that $\mathbf{D} = \mathbf{O}$ if they be separated by a space-like distance, one is led to the general results that for integral spin quantisation according to F.D. statistics is not possible, and that for half-integral spin there is no algebraic contradiction in either statistics being satisfied, but the removal of the negative energy difficulty is not possible if one uses the E.B. statistics. These results are purely negative in character, but the actual carrying through of the quantisation shows that for half-integral and integral spins a satisfactory theory can be obtained by quantising respectively with the F.D. and E.B. statistics. Thus, the connection between spin and statistics is to be considered as one of the most important physical applications of the Lorentz group.

A deeper insight into the role of $\mathbf{L}_4$, the introduction of the notions of abstract algebra in dealing with elementary particles, and also the need for considering invariance under subgroups like ($\mathbf{L}_4$, $\mathbf{PTL}_4$) more general than $\mathbf{L}_4$ all result when we come to the consideration of a Dirac type of equation of the first order, which might be thought of as a transition from the field to the particle aspect of quantum theory. In order that a theory based on a wave equation set up for establishing the connection between spin and statistics may represent particles of a single spin, it is necessary to assume, besides the symmetry of the spinor in the dotted and undotted indices, that the spinors $p^{\dot{\nu}\rho}a^{\dot{\lambda}\dot{\mu}\ldots}_{\rho\dot{\delta}\ldots}$ and $p_{\dot{\nu}\delta}a^{\dot{\nu}\dot{\mu}\ldots}_{\lambda\rho\ldots}$ (where $p^{\dot{\nu}\rho}$ is the gradient spinor) should also be symmetrical. This makes it possible to go from the second order wave equation to a system of two first order equations of the type

$$\left.\begin{aligned} p^{\dot{\nu}\rho}a^{\dot{\lambda}\dot{\mu}\ldots}_{\rho\dot{\delta}\ldots} &= \chi b^{\dot{\nu}\dot{\lambda}\dot{\mu}\ldots}_{\dot{\delta}\ldots} \\ p_{\dot{\nu}\rho}b^{\dot{\nu}\dot{\lambda}\dot{\mu}\ldots}_{\dot{\delta}\ldots} &= \chi a^{\dot{\lambda}\dot{\mu}\ldots}_{\rho\dot{\delta}\ldots} \end{aligned}\right\} \qquad (7)$$

where $h\chi$ is the rest mass of the particle, and the spinor b satisfies the same conditions of symmetry as a. The cases where a has $2k$ undotted and $2k-1$ dotted indices, or $2k$ dotted and $2k$ undotted indices according as the spin is half-integral or integral respectively are specially simple, and denoting these spinors by $a^{(0)}$ and $b^{(0)}$, they have the property of going over into each other by reflections of space-time. In the integral case $a^{(0)} = b^{(0)}$, and in the half-integral case $a^{(0)} \rightleftarrows b^{(0)}$ under reflections, so that together they form a system invariant under ($\mathbf{L}_4$, $\mathbf{PTL}_4$). The first order wave equations in them are said to be of the Dirac particle type. Using the general result of semi-simple Lie groups (of which $\mathbf{L}_4$ is a particular example) that if the matrix commuting with all the matrices of an infinitesimal product representation is brought to the diagonal form, the product representation is

simultaneously split up into its irreducible components, it can be shown that the above type of equations can be reduced to a type involving only one spinor index, *viz.*,

$$\left.\begin{aligned} p^{\dot{\nu}\rho}\psi_{\rho}{}^{\mathrm{A}} &= \chi\psi^{\dot{\nu}\mathrm{B}} \\ p_{\dot{\nu}\rho}\psi^{\dot{\nu}\mathrm{B}} &= \chi\psi_{\rho}{}^{\mathrm{A}} \end{aligned}\right\} \tag{8}$$

where A and B indicate that ψ involves magnitudes like $A_s^{\dot{r}}$ and $B_j^{\dot{i}}$, and the equations are to be treated as matrix equations. Finally, the two equations can be combined into one single equation, the famous Dirac equation representing the particle aspect, *viz.*,

$$\partial_\mu\beta_\mu\psi + \chi\psi = 0;\ \left(\partial_\mu = \frac{\partial}{\partial x_\mu},\ \mu = 1, 2, 3, 4\right) \tag{9}$$

where for the case of spin $\frac{1}{2}$ the Dirac matrices satisfy the commutation relations

$$\tfrac{1}{2}(\beta_\mu\beta_\nu + \beta_\nu\beta_\mu) = \delta_{\mu\nu}. \tag{10}$$

In virtue of these relations, the system of the sixteen numbers 1, β_μ, $\beta_\mu\beta_\nu$, $\beta_\lambda\beta_\mu\beta_\nu$ and $\beta_1\beta_2\beta_3\beta_4$ form a hypercomplex system, the Dirac algebra. As is well known the theorems relating to representations of a finite group can be extended to group rings and hence also to an algebra satisfying certain conditions. Applying the theorems which hold in the special case of a semi-simple algebra of which the Dirac algebra is a particular case, it is very easy to prove that that this algebra has only one irreducible representation of order 4, showing that the Dirac equation is unique but for equivalence. I have shown sometime back that the question of setting up a Dirac type of wave equation for particles of spin greater than half can also be dealt with on the basis of the invariance of the wave equation under L_4.

3. Charge Invariance and Gauge Invariance

Another remarkable feature of the Dirac theory is that it has led to the concept of an anti-particle as a hole in a negative energy state, and thus introduced a new type of transformation in physics, the so-called particle-anti-particle conjugation, which we will denote here as C. In the case of a charged particle this transformation merely amounts to a change in the sign of the electric charge, and is referred to as *charge-conjugation*. One is thus led to consider the question of invariance of spinor fields under the transformation C, which, amounting to the replacement of a function by its complex conjugate, is not a linear operator, and is therefore different from the Lorentz

type. As mentioned earlier in § 2, the introduction of the notion of charged fields in relativistic quantum theory amounts to the setting up of a current four-vector by dividing the field quantities into $\mathrm{U}(x)$, $\mathrm{U}^*(x)$ and $\mathrm{V}(x)$ by assuming the invariance of the Lagrangian against gauge transformations defined by

$$\bar{\mathrm{U}}(x) \rightarrow \bar{\mathrm{U}}(x)\, e^{ia};\ \bar{\mathrm{U}}^*(x) \rightarrow \bar{\mathrm{U}}^*(x)\, e^{-ia} \tag{11}$$

(a being a constant when no external fields are present), since such a transformation leads to the possibility of setting up the current vector by expressing the non-measurability of the phase of the complex wave function of a charged particle. The field with a complex U can be written as equivalent to two real fields $\mathrm{V} = \mathrm{V}^*$ and $\mathrm{W} = \mathrm{W}^*$ with

$$\bar{\mathrm{U}} = \frac{1}{\sqrt{2}}(\mathrm{V} + i\mathrm{W});\ \bar{\mathrm{U}}^* = \frac{1}{\sqrt{2}}(\mathrm{V} - i\mathrm{W}) \tag{12}$$

the numerical factor being introduced for the sake of convenience in quantisation. In the particular case of a particle of spin $\frac{1}{2}$ (*e.g.*, an electron), Pauli has shown that this splitting into two real fields is possible, and that one can set up a Lorentz-invariant ordering between the solutions of Dirac's equation with positive and negative frequency, denoted by u_+ and u_-, such that if the former satisfies the wave equation with charge $+e$, the latter satisfies with charge $-e$. The pair of spinors u_+ and u_- can be easily seen to be of the type of spinors $a^{(0)}$ and $b^{(0)}$ considered under (7) going into each other under space-time reflections in this case of spin $\frac{1}{2}$. Thus the Dirac spinor u_ρ constituting this pair u_+ and u_- can be considered as an irreducible representation of the group (L_4, PTL_4) with the further property of being invariant under C also, and it must be emphasised that this is a consequence of the spin of the electron being half-integral, and hence its satisfying the F.D. statistics. This notion of invariance under C, or that of charge conjugate states can be extended to higher spins also by working with field quantities $\psi_{\rho_1\rho_2\ldots\rho_n}$ which transform like products of Dirac spinors under L_4, and these quantities are called *undors*, u_ρ itself being an undor of rank one. Pauli and Belinfante have shown that in the general case also, one can build up a theory for these undors which is charge-invariant provided one works with a q-number theory.

The special cases of particles of zero charge (neutral particles), and zero mass can be considered under (12) and (11) respectively. In the former case, one can make an abbreviation of the theory due to Majorana by striking out W and its bracket relations, *i.e.*, identifying the charge conjugate states. For the case of general spin, this would amount to considering self-con-

jugated undors or what are called *neutrettors*, and a consistent theory can be built for these field quantities also. In the latter case of zero mass, the gauge transformation (11) with α a function of space-time, and an additional type of gauge transformation superimposed on it enable the building-up of a theory leading to the physically significant result that a particle of zero rest mass has only two independent and really different plane waves for a specified wave number and frequency.

4. Parity, Charge Conjugation and Time Reversal

In view of the importance of interactions between several types of particles in present-day physics, Pauli has recently returned to the questions of invariance under charge conjugation, space-time reflections, and L_4, and also the spin-statistics connection. Denoting the particle-anti-particle conjugation by AC (which we have denoted by C), the space-time reflection as a weak reflection WR, and the combination of WR with AC as a strong reflection SR, he has derived on the basis of interactions between particles in the simplest cases of spins 0, $\frac{1}{2}$ and 1, the following theorems:—

(*a*) The WR holds whether or not the normal connection between spin and statistics is assumed.

(*b*) The transformation law for a quantity with respect to L_4 does not determine uniquely its behaviour for WR; and the invariance with respect to WR imposes further restrictions upon the Lagrangian density of the interactions, besides its invariance for L_4.

(*c*) The SR is uniquely determined as a consequence of L_4 and the spin-statistics connection.

The remarkable result (*c*) that the SR follows from more general results than the WR or AC is referred to as the *Pauli-Ludërs theorem*, and throws light on some problems that have recently arisen in connection with the interaction of elementary particles. As SR is the product of WR and AC, it follows immediately from the above theorem that the results (*a*) and (*b*) are also true for AC with the same additional restrictions imposed on the interaction Lagrangian density, and that the transformation of a certain kind of spinor or tensor for WR uniquely determines its transformation for AC. As an illustration of the Pauli-Ludërs theorem, we might mention the theory of undors dealt with in the previous Section.

Although in the above considerations of Pauli, the conservation properties of P and T have not been separately taken into account, it can be shown, as has been done by Lee, Oehme and Yang (*Phys. Rev.*, 1957, **106**,

340), that we can derive, from (*c*), above some general results regarding conservation under the parity P, the pure time reversal T, and the charge conjugation C. Noting that SR is a combination of C, P and T, these authors have considered the transformation properties (in the Schrodinger representation) of wave functions of the doubly quantised spin fields (both integral and half-integral) under the operations P, C and T with these transformations involving phase factors η_P, η_C, η_T of absolute value unity. Working with a local Hermitian operator invariant under L_4, they have shown that the Pauli-Ludërs theorem is equivalent to the statement that there always exists a choice of η_P, η_C and η_T such that (A) H commutes with the product of the operators P, C and T taken in any order, and (B) if this choice does not make H commute with P, for example, then no other choice does and the theory is not invariant under P, and the same holds for C and T also. Of course, (B) includes also the possibility that the choice of phases made under (A) may make H commute with P. The statements (A) and (B) constitute the *CPT-theorem* which is thus a simple consequence of the Pauli-Ludërs theorem. It can be shown from the CPT-theorem that if one of the operators P, C and T is not conserved, at least one other also must not be conserved. Thus, there are five possibilities of conservation or non-conservation of P, C, T as indicated in the table below:—

No.	Non-conserved operators	Conserved operators	
1	..	P, C, T	
2	C, T	P, CT, TC	(13)
3	P, T	C, PT, TP	
4	C, P	T, CP, PC	
5	P, C, T	PCT and permutations	

The CPT-theorem of Lee and Yang has recently obtained a brilliant confirmation in experimental results relating to non-conservation of parity in weak interactions. Considering such an interaction like the emission of neutrinos in β-decay, the experiments of Dr. Wu and collaborators at Columbia University in the β-decay of Cobalt 60 have shown that parity is not conserved in the interaction. Thus, in a correct theory of the neutrino ν^0 (defined to be a particle in the +ve energy state), its spin is always parallel to its momentum, while the spin of an anti-neutrino (defined as a hole in a

–ve energy state) is always anti-parallel to its momentum (that of ν^0). Thus the spin and velocity of ν^0 represent the spiral motion of a right-handed screw, while the spin and velocity of ν^0 represent the spiral motion of a left-handed screw. The theory also shows that there is no invariance under C, and hence as indicated in table (13), there may be invariance under CP, and also under T, or T also may be violated with invariance however under PCT.

Interactions among elementary particles can be classified into three categories, the strong, the electromagnetic, and the weak interactions, the first type having intensities around 1 to 10^{-1}, the electromagentic ones having 10^{-2} and the weak ones having intensities ranging from 10^{-12} to 10^{-14}, and the wide gap separating the third category from the first two is also a remarkable fact still requiring an explanation. Denoting the K-mesons and hyperons as "*strange*" particles, another striking experimental observation is that while the production of strange particles falls into the first category, their decay falls into the third. Regarding the status of the CPT-theorem for strong interactions, experimental evidence indicates that P is conserved in such interactions, and it is usual to assume that C and T also are conserved, so that the first row of table (13) represents strong interactions. Making this assumption, and considering a Hamiltonian which is the sum of a strong part H_s and a weak part H_w, with the former invariant under C, P and T, and both parts invariant under L_4, one can derive interesting results throwing light on the interrelations between non-conservation of C, P and T.

The question of invariance under the transformations C, P, and T can thus be considered as a deeper analysis of the role of the Lorentz group in physical applications, and it becomes necessary and important to examine if many of the recently discovered phenomenological laws of symmetry or invariance, which hold for particle interactions, can be elucidated on the basis of this analysis. One such invariance law is the conservation of the number of nucleons, which necessitates the assignment of a "*heavy particle quantum number*" N to all elementary particles. A consistent assignment is possible if one puts $N = 0$ for the light particles and the L-mesons, $N = \pm 1$ for the nucleons and anti-nucleons respectively, $N = 1$ for the hyperons, and $N = 0$ also for the K-meson class. Another is the conservation of charge in all interactions. A third conservation law is that of "*strangeness*" S which is noticed to hold in the case of the strong and electromagnetic interactions only, if one assigns $S = 0$ to the nucleons and π-mesons, $S = 1$ to K^0 and K^+, $S = -1$ to K^-, K^{-0}, $\overline{K}^0$, Σ^+, Σ^0 and Σ^-, $S = -2$ to the heaviest hyperon $\equiv^-$. The weak interactions violate this strangeness conservation. Finally taking the strong interactions only into consideration, it is found

that the third component τ_3 of the isotopic spin quantum number (given by the Pauli 2×2 matrices) is invariantly connected with N and S by the relation

$$\tau_3 = Q - \frac{N}{2} - \frac{S}{2}, \tag{14}$$

where Q is the charge expressed in multiples of $|e|$. The elucidation of these laws is still an open question. A mention may finally be made of the so-called τ-θ puzzle which appears to have recently received a satisfactory explanation on the basis of the non-conservation of parity in weak interactions. These two strange K-mesons τ^+ and θ^+ have closely identical masses and life-times, but only differ in having different decay processes into π-mesons (the mesons which are responsible for the main features of nuclear forces), *viz.*,

$$\left.\begin{aligned} \tau^+ &\rightarrow \pi^+ + \pi^+ + \pi^- \\ \theta^+ &\rightarrow \pi^+ + \pi^0 \end{aligned}\right\} \tag{15}$$

Both these interactions are weak since S is not conserved in them, and non-conservation of parity in such interactions makes it possible to think of τ^+ and θ^+ as one K-particle having a definite parity on production, but decaying into various parities. Also the mass degeneracy of τ^+ and θ^+ can be explained by assuming that they have the same spin but opposite parity, *i.e.*, they are related by an invariance law called the "*parity conjugation*" denoted by C_P, or in other words, that they are parity doublets. C_P would commute with H_s, but not with H_w and one could thus explain the mass degeneracy. Considering the strange particles with odd values of S like the τ and θ, a general law has been established that particles of odd strangeness given by (14) must be parity doublets, while for even S, the operation C leaves the parity invariant, *i.e.*,

$$C_P P - (-1)^S P C_P = 0. \tag{16}$$

5. CONCLUDING REMARKS

While the questions discussed in the previous Section show that a deeper knowledge of the representations of the full Lorentz group, and its several subgroups, including perhaps the infinite representations also, may yield useful results in interpreting the conservation laws of nature, it is clear that this alone is not sufficient. It has to be correlated with laws relating to charge conjugation, general gauge transformations, laws of isotopic spin, and perhaps others. It also appears that no need has been felt so far radically to modify the quantum principles in the application to elementary particles. Thus, while Bohr's theory of complementarity

can be said to have remained inviolate, Einstein's principle of relativity appears to be undergoing modifications in the method of applying it to physical problems. Suggestions of this nature have also been recently made that the inconsistencies discovered in the quantum theory of elementary particles, specially the quantum electro-dynamics, wherein the photon appears, can perhaps be removed when weak gravitational effects of Einstein's general relativity theory are properly taken into consideration. For example, the cosmological asymmetry which results as a violation of parity is perfectly compatible with Riemann space-time of ordinary general relativity. These ideas have given rise to a spate of theories devoted to a re-examination of general relativity. One such theory starts with the assumption that particles with a spin always generate a gravitational field, another attempts to build-up a theory of gravitation by using the neutrino theory, and so on.

An exciting period is now clearly before the experimental as well as the theoretical physicist due to the discovery of the phenomenon of non-conservation of parity, which has resulted from the circumstance that Nature uses simple but strange representations of the Lorentz group to characterise the strange particles.

SUMMARY

The role of special relativity, based on the restricted Lorentz group L_4 consisting of rotations in space-time, in the earlier development of quantum theory, in the connection between spin and statistics established by Pauli, and in Dirac's theory of the electron is briefly indicated. The theory of undors is pointed out as an example where, besides invariance under L_4, invariance under charge-conjugation and space-time reflections also is satisfied.

The Pauli-Ludërs theorem taking into account the interactions between elementary particles, and the subsequent work of Lee and Yang relating to parity, charge-conjugation and time-reversal are explained, and cited as examples of general representations of the Lorentz group.

SUR LA RÉSOLUTION DU PROBLEME DE RAMAN-DEY

By S. A. Dianine

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§ 1

Vers la fin du siècle passé les constructions différentes et assez nombreuses, entreprises pour fournir aux musiciens des instruments d'un genre essentiellement nouveau—les pianos magnétiques—furent cause de quelques publications théoriques concernant les lois des mouvements très petits " d'une corde ferromagnétique dans " le champ d'un aimant, mouvements effectués à l'aide d'un interrupteur.[1]

Au commencement du siècle courant furent aussi étudiées les vibrations d'une corde faisant partie d'un circuit animé d'un courant alternatif et située dans le champ de deux aimants; la théorie des vibrations pareilles devint nécessaire pour la construction des galvanomètres à corde.[2]

L'investigation d'une autre forme du problème ici abordé, notamment,—l'étude des vibrations d'une corde dans un champ électromagnétique variable, a été entamée à peu près, vers les années 1912–15. Cette investigation montra la nécessité de prendre en considération l'influence du mouvement de la corde sur la force perturbatrice du champ. La priorité dans l'étude de ce dernier problème appartient aux physiciens hindoux—M. M. C. V. Ramàn et Ash. Dey qui publièrent ses travaux concernant le problème en question en 1915 et en 1917.[3]

Les savants mentionnés ont pris, pour calculer le mouvement étudié, l'équation aux dérivées partielles:

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[1] Voir, par exemple, G. Klinkert. "Die Benegung elektromagnetisch erregter Saiten" *Wiedemanns Annalen der Physik und Chemie*, Bd. LXV (1898), s. 849–72. *Comp.*, aussi, les dictionnaires instrumentologiques.

[2] P. Hertz, "Zur Theorie des Saitengal vanometers," *Zeitschrift fur Mathematik und Physik*, Bd. 58 (1910), s. 1–71.

[3] Raman, C. V., "On a Motion in a Periodic Field of Force," *Phil. Mag.*, 1915, **29**(6).

Raman, C. V. and Dey, Ash, "The Maintenance of Vibrations by a Periodic Field of Force," *Phil. Mag.*, 1917, **34**(6).

$$\frac{\partial^2 u}{\partial t^2} - a^2 \frac{\partial^2 u}{\partial x^2} = u(t) \cdot \nu(x) \cdot \rho(u). \tag{1}$$

Ils proposèrent de déterminer la fonction inconnue u à l'aide des approximations successives; la convergence de ces approximations n'était pas étudiée dans leurs travaux cités.

Il me semble juste de lier le problème considéré avec les noms de ses premiers investigateurs; je donnerai donc, dans les lignes suivantes, l'appellation de *problème de Raman-Dey* à celui de la détermination d'une fonction u satisfaisant à l'équation

$$\frac{\partial^2 u}{\partial t^2} - a^2 \frac{\partial^2 u}{\partial x^2} = f(x, t)\, \rho(u) \tag{2}$$

et à quelques conditions accessoires.

L'auteur de cet article commença l'étude du problème en question vers l'année 1926. J'ai dirigé pendant les années 1926, 1927 et 1928, étant à la fois mathématicien et musicologue, les travaux d'un groupe de jeunes savants qui avaient pour but d'élaborer la théorie et les principes techniques de la construction d'un piano au timbre variable.

N'ayant pas encore pris alors notion des travaux cités de Raman et Dey, j'ai découvert, indépendamment, la nécessité de donner à l'équation du problème une forme non linéaire: j'ai choisi pour ça l'équation:

$$\frac{\partial^2 u}{\partial t^2} + 2\delta \frac{\partial u}{\partial t} - a^2 \frac{\partial^2 u}{\partial x^2} = \mu(t)\, \gamma(x)\, \rho(u), \tag{3}$$

c'est à dire l'équation (1) transformée par l'introduction du membre représentant la force du frottement intérieur.

J'ai proposé de chercher la fonction u sous la forme d'une série de polynomes trigonomètriques; l'introduction de la série mentionnée était purement formelle car je n'ai pas fixé les conditions de sa convergence.[4]

Les travaux *plus* récents, consacrés au probléme en question, ne sont pas nombreux.

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[4] S. A. Dianine, "Sur l'intégration de l'équation des vibrations d'une corde ferromagnétique dans un champ magnétique variable," *Mem. Scientif. du Laboratoire Exp. Electrotechnique de Leningrade, fase.* 1929, 9, pp. 2037 (En russe).

Le rapport concernant les experiments *voir* dans mon article, "Sur les vibrations d'une corde sous l'influence des forces electromagnetiques," *Ibidem*, pp. 5–19 (En russe).

En 1927 le géomètre allemand Lichtenstein a, démontré l'existence de la solution d'une équation non linéaire contenant l'équation (2) comme un cas particulier; l'auteur a supposé que la solution cherchée satisfait aux conditions accessoires habituellement admises dans le problème classique des cordes vibrantes. Cette démonstration a été effectuée à l'aide d'une suite infinie d'approximations ayant la forme d'équations intégrales non linéaires. Un calcul effectif des grandeurs physiques par une telle méthode est, pour ainsi dire, ā peu près impossible.[5]

En se servant d'une substitution fonctionnelle et des séries de puissances j'ai démontré (en 1937) l'existence de la solution de l'équation généralisée (3), satisfaisante aux conditions aux limites et aux conditions initiales. La méthode que j'ai employé permet de calculer la fonction inconnue mais elle n'est pas commode pour découvrir les propriétés de la solution, intéressantes pour les physiciens.

Ayant en vue les applications possibles de la théorie du probléme de Raman-Dey, j'ai trouvé utile d'inventer une méthode qui permettrait de représenter la solution de ce problème sous une forme plus ou moins simple.

En tenant oompte de l'indétermination analytique de la fonction $\rho(u)$[6] et de sa forme déduite des expériments à l'aide de l'interpolation, j'ai constaté la possibilité de ramener, dans quelques cas, particuliers la solution du probléme á l'intégration de l'équation connue de Liouville.

Les paragraphes suivants ont pour but de montrer que cette assertion est effectivement valable.

§2

Les résultats de mesurages nombreux, effectués par les membres du groupe mentionné au §1 et quelques résultats analogues que j'ai obtenu plus tard (en 1939) dans un autre laboratoire me permettent de représenter qualitativement le facteur $\rho(u)$ figurant dans les secondes parties des équations (1), (2), (3) par la courbe TSQ (Fig. 1).[7]

Cette figure nons montre la possibilité de représenter approximativement la fonction $\rho(u)$ par une formule exponentielle:

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[5] *Crelle's Journal fur reine und angewandte Mathematik*, 1927.

[6] Ou l'absence d'une représentation analytique de cette grandeur qui pourrait figurer dans une équation sans la rendre trop compliquée.

[7] Nous avons en vue le cas où les deux pôles d'un électroaimant sont situés du même côté de la corde de la maniére indiquée sur la figure 2.

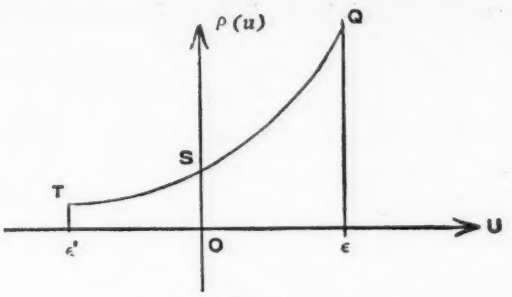

FIG. 1

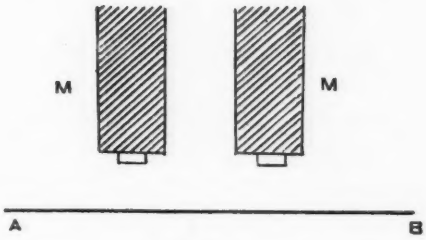

FIG. 2

$$\rho(u) \cong \mathrm{R}e^{\kappa u} - \mathbf{D}. \tag{4}$$

Dans cet article je me bornerai à l'étude des cas où la constante **D** est supposée égale à zéro.

§ 3

Il est bien connu que Joseppe Liouville a obtenu jadis pour l'équation portant aujourd'hui son nom:

$$\frac{\partial^2 w}{\partial \xi \partial \eta} = e^{\kappa w} \tag{5}$$

une solution avec deux fonctions arbitraires A_1, A_2, exprimée par la formule:

$$e^{\kappa w} = \frac{2A_1'(\xi)\,A_2'(\eta)}{\kappa\,[A_1(\xi) + A_2(\eta)]^2}. \tag{6}$$

En faisant la substitution:

$$\xi = x + at, \quad \eta = x - at,$$

on déduit de l'équation (5):

$$\frac{\partial^2 w}{\partial t^2} - a^2 \frac{\partial^2 w}{\partial x^2} = -4a^2 e^{\kappa w}, \tag{7}$$

où la fonction w est déterminée, vu la formule (6), par l'égalité suivante

$$w = \frac{1}{\kappa}\{ln2 - ln\kappa + ln\,[A_1'(x+at)\,A_2'(x-at)] - 2ln\,[A_1(x+at) + A_2(x-at)]\}. \tag{8}$$

En posant $w = -w_1$, $-\kappa = r$, on trouve:

$$\frac{\partial^2 w_1}{\partial t^2} - a^2\frac{\partial^2 w_1}{\partial x^2} = 4a^2 e^{rw_1},$$

$$w_1 = \frac{1}{\lambda}\{ln2 - ln(-\lambda) + ln\,[A_1'(x+at)\,A_2'(x-at)] + - 2ln\,[A_1(x+at) + A_2(x-at)]\}.$$

En reprenant les désignations w, κ au lieu de w_1, λ et en remarquant que:

$$-ln(-\lambda) + lns = -ln\lambda - ln(-1) + ln(-1) + ln(-s) = -ln\lambda + ln(-s),$$

on reçoit les formules:

$$\frac{\partial^2 w}{\partial t^2} - a^2\frac{\partial^2 w}{\partial x^2} = 4a^2 e^{\kappa w} \tag{9}$$

$$w = \frac{1}{\kappa}\{ln2 - ln\kappa + ln\,[-A_1'(x+at)\,A_2'(x-at)] + - 2ln\,[A_1(x+at) + A_2(x-at)]\}. \tag{10}$$

Considérons maintenant une nouvelle inconnue u, déterminée par l'égalité:

$$w = u + \frac{1}{\kappa}ln\theta,$$

où θ est une certaine fonction donnée de x et t.

A l'aide des formules (9), (10) nous trouvons aisément que l'équation:

$$\frac{\partial^2 u}{\partial t^2} - a^2\frac{\partial^2 u}{\partial x^2} = 4a^2\theta e^{\kappa u} - \frac{1}{\kappa}\left(\frac{\partial^2 ln\theta}{\partial t^2} - a^2\frac{\partial^2 ln\theta}{\partial x^2}\right) \tag{11}$$

admet l'intégrale:

$$u = \frac{1}{\kappa}\left\{ln2 - ln\kappa + ln\left[-\frac{A_1'(x+at)\,A_2'(x-at)}{\theta(x,t)}\right] + - 2ln\,[A_1(x+at) + A_2(x-at)]\right\}. \tag{12}$$

Remarque.—Signalons le cas particulier, où la fonction θ est déterminée par l'égalité:

$$\theta(x, t) = \mathrm{M}(x + at)\, N(x - at). \tag{13}$$

Dans ce cas on constate que *l'intégrale générale de l'équation*:

$$\frac{\partial^2 u}{\partial t^2} - a^2 \frac{\partial^2 u}{\partial x^2} = 4a^2 \mathrm{M}(x + at)\, \mathrm{N}(x - at)\, e^{\kappa u} \tag{14}$$

qui est une forme particulière de l'équation (2) *du problème de Raman-Dey est donnée par la formule suivante*:

$$u = \frac{1}{\kappa}\left\{ln2 - ln\kappa + ln\left[-\frac{\mathrm{A_1}'(x + at)\,\mathrm{A_2}'(x - at)}{\mathrm{M}(x + at)\,\mathrm{N}(x - at)}\right] + \right.$$

$$\left. - 2ln\left[\mathrm{A_1}(x + at) + \mathrm{A_2}(x - at)\right]\right\}. \tag{15}$$

§ 4

Considérons maintenant le problème de Cauchy relatif aux équations (11), (14). Sa résolution se réduit évidemment à la détermination des fonctions arbitraires dans la formule (12) à l'aide des conditions initiales:

$$u_{t=0} = \mathrm{F}(x), \tag{16}$$

$$\left(\frac{\partial u}{\partial t}\right)_{t=0} = \mathrm{G}(\infty). \tag{17}$$

Posons, ce qui est plus commode pour les calculs:

$$\mathrm{A_1}(s) = \mathrm{A}(s),$$

$$-\mathrm{A_2}(s) = \mathrm{B}(s).^{8} \tag{18}$$

En introduisant encore les désignations:

$$\theta(x_1\, 0) = \zeta(x)^{9} \tag{19}$$

$$\kappa \mathrm{F}(x) + ln\left[\frac{k\zeta'(x)}{2}\right] = \Phi(x), \tag{20}$$

on obtient, en vertu des formules (12) [resp. (15)] et (16):

$$\frac{\mathrm{A}'(x)\,\mathrm{B}'(x)}{[\mathrm{A}(x) - \mathrm{B}(x)]^2} = e^{\Phi(x)}. \tag{21}$$

[8] Nous supposerons toujours que $\mathrm{A}(s) \neq \mathrm{B}(s)$.

[9] Nous supposons que $\zeta'(x) > 0$.

En formant $\partial u/\partial t$ et en posant, pour abréger l'écriture:

$$\frac{\kappa G(x)}{\alpha} + \frac{1}{\alpha\zeta(x)}\left[\frac{\partial\theta(x,t)}{\partial t}\right]_{t=0} = \Psi(x), \tag{22}$$

on déduit, à l'aide de (17):

$$\frac{A''(x)}{A'(x)} - \frac{B''(x)}{B'(x)} - \frac{2[A'(x)+B'(x)]}{A(x)-B(x)} = \Psi(x). \tag{23}$$

La détermination des fonctions A, B est donc réduite à l'intégration d'un système d'équations différentielles ordinaires (21), (23).

En posant:

$$A'(x)\,B'(x) = D^2(x), \tag{24}$$

il vient:

$$B'(x) = \frac{D^2(x)}{A'(x)}. \tag{25}$$

La formule (21) nous donne:

$$A(x) - B(x) = \pm e^{-\frac{1}{2}\Phi(x)} D(x) = H(x)\,D(x),^{10} \tag{26}$$

$$B'(x) = A'(x) - [H(x)\,D(x)]'. \tag{27}$$

A' l'aide des égalités (25), (27) on trouve:

$$(A')^2 - (DH)'A' - D^2 = 0. \tag{28}$$

On reçoit maintenant aisément les formules:

$$A' = \frac{(DH)' \pm \sqrt{[(DH)']^2 + 4D^2}}{2}, \tag{29 a}$$

$$B' = \frac{-(DH)' \pm \sqrt{[(DH)']^2 + 4D^2}}{2}, \tag{29 b}$$

$$A' + B' = \pm\sqrt{[(DH)']^2 + 4D^2}. \tag{29 c}$$

En tenant compte de ces égalités et de la formule (26) et en introduisant une nouvelle fonction inconnue Ω par la formule:

$$\frac{(DH)'}{D} = \Omega, \tag{30}$$

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[10] La désignation $\pm e^{\frac{1}{2}\Phi(x)} = H(x)$ est introduite pour abréger l'écriture.

on réduira l'équation (23) à la forme suivante:

$$\left[ln\left(\frac{\pm\sqrt{\Omega^2+4}+\Omega}{\pm\sqrt{\Omega^2+4}-\Omega}\right)\right]' \mp \frac{2\sqrt{\Omega^2+4}}{\mathrm{H}} = \Psi.$$

Après quelques transformations simples il viendra:

$$\Omega' = \frac{\Omega^2+4}{\mathrm{H}} + \psi\sqrt{\Omega^2+4}. \tag{31}$$

$$\left(\text{Tci on a posé: } \pm\frac{\Psi}{2} = \psi\right). \tag{32}$$

Remarque.—L'équation (31) s'intégre par des quadratures, si:

$$\frac{1}{\mathrm{H}} = p\kappa, \quad \psi = q\kappa,$$

où p, q sont des constantes, et $\kappa = \kappa(x)$ une fonction de son argument.

En se proposant de former l'expression de u en fonction de Ω, on trouve, en tenant compte des équations (30), (29 *a*), (29 *b*):

$$\mathrm{D} = \frac{\mathrm{C}_1}{\mathrm{H}} e^{\int_a^x \frac{\Omega}{\mathrm{H}} d\zeta}, \tag{33}$$

$$\mathrm{A} = \frac{\mathrm{C}_1}{2}\int_\beta^x e^{\int_a^\lambda \frac{\Omega}{\mathrm{H}} d\zeta} \frac{\pm\sqrt{\Omega^2+4}+\Omega}{\mathrm{H}} d\lambda + \mathrm{C}_2, \tag{34 *a*}$$

$$\mathrm{B} = \frac{\mathrm{C}_1}{2}\int_\beta^x e^{\int_a^\lambda \frac{\Omega}{\mathrm{H}} d\zeta} \frac{\pm\sqrt{\Omega^2+4}-\Omega}{\mathrm{H}} d\lambda + \mathrm{C}_3.^{11} \tag{34 *b*}$$

Enfin, en vertu des égalités (12) et (18), on reçoit la formule:

$$u = \frac{1}{\kappa}\left\{ln2 - ln\kappa + \int_a^{x+at}\frac{\Omega}{\mathrm{H}}d\zeta + \int_a^{x-at}\frac{\Omega}{\mathrm{H}}d\zeta\right.$$

$$\left. + ln\left\{\frac{[\pm\sqrt{\Omega^2(x+at)+4}+\Omega(x+at)]\,[\pm\sqrt{\Omega^2(x-dt)+4}-\Omega(x-at)]}{\theta(x,t)\,H(x+at)\,\mathrm{H}(x-at)}\right\}\right.$$

[11] En transformant l'égalite' (26) à l'aide de (34 *a*), (34 *b*), on découvre l'existence de la relationsui vante entre les constantes C_1, C_2, C_3:

$$- 2ln\left[e^{\int_a^{x+at} \frac{\Omega}{H} d\xi} + e^{\int_a^{x-at} \frac{\Omega}{H} d\xi} \pm \int_{x-at}^{x+at} e^{\int_a^{\lambda} \frac{\Omega}{H} d\xi} \frac{\sqrt{\Omega^2+4}}{H} d\lambda \right] \Bigg\}. \qquad (35)$$

Ainsi nous avons réduit la résolution du problème de Couchy pour l'équation (14) *du type Raman-Dey et pour l'équation* (11) *un peu généralisées à l'intégration de l'équation différentielle ordinaire du premier ordre* (31) *et aux quadratures.*

$$C_2 - C_3 = C_1 e^{\int_\beta^\alpha \frac{\Omega}{H} d\xi}.$$

Première remarque.—Signalons, les conditions qui doivent être remplies si la fonction u déterminée par la formule (35) doit être une fonction réelle.

(*a*) Nous devons admettre l'existence d'une solution réelle Ω de l'équation différentielle (31), solution finie et déterminée dans un certain intervalle des valeurs de la variable indépendante.

(*b*) Cette condition remplie, la fonction u déterminée par la formule (35), représentera une fonction réelle et finie des arguments x, t, si les arguments des logarithmes dans la seconde partie de la formule mentionnée sont finis, positifs et différents de zéro.

Il est aisé de constater que l'argument du *premier* logarithme (en allant de la gauche à la droite) satisfera à la condition énoncée, si

$$\theta(x, t) > 0^{12}$$

car les expressions:

$$[\pm \sqrt{\Omega^2(x+at)+4} + \Omega(x+at)],\ [\pm \sqrt{\Omega^2(x-at)+4} - \Omega(x-at)]$$

possèdent toujours les mêmes signes et ne sont pas égales au zéro, et le produit: $H(x+at)\,H(x-at)$ satisfait à la relation évidente:

$$H(x+at)\,H(x-at) = e^{-\frac{1}{2}[\Phi(x+at)+\Phi(x-at)]} > 0.$$

L'argument du *second* logarithme peut être transformé dans un carré d'une grandeur réelle: il n'est donc jamais négatif. Il nous reste á reconnaître, sous quelles conditions cet argument est différent de zéro.

[12] Cette condition contient, comme un cas particulier, l'inégalité $\xi(x) > 0$ postulée plus haut

Les quantités:

$$e^{\int_a^{x+at} \frac{\Omega}{H} d\xi}, \quad e^{\int_a^{x-at} \frac{\Omega}{H} d\xi}.$$

Sont toujours finies et positives. Quant à la fonction:

$$e^{\int_a^{\lambda} \frac{\Omega}{H} d\xi} \frac{\sqrt{\Omega^2 + 4}}{\pm |H|}$$

dans la troisième intégrale, on peut toujours y choisir le signe de $|H|$ coincidant avec le signe devant l'intégrale et rendre ainsi ce membre positif.

En résumant la discussion, nous pouvons donc dire que u sera une grandeur réelle et finie quand le postulat (a) est valable et quand ont lieu les conditions:

$$\theta(x, t) > 0, \tag{36}$$

$$\pm \int_{x-at}^{x+at} e^{\int_a^{\lambda} \frac{\Omega}{H} d\xi} \frac{\sqrt{\Omega^2 + 4}}{\pm |H|} d\lambda = + \int_{x-at}^{x+at} e^{\int_a^{\lambda} \frac{\Omega}{H} d\xi} \frac{\sqrt{\Omega^2 + 4}}{|H|} d\lambda. \tag{37}$$

Deuxième remarque.—Il est aisé de fixer les conditions sous lesquelles la fonction u, déterminée par la formule (35), représente éffectivement une solution du problème étudié. Il est évident que pour cela hormis les conditions énoncées dans la remarque précédente, on doit admettre, pour les fonctions Ω, H, θ, l'existence de leurs dérivées partielles *du* premier et *du* second ordre.

Troisiéme remarque.—En admettant des relations particulières entre les fonctions A et B, par exemple, en introduisant dans nos calculs une des deux égalités:

$$A = B + \gamma \qquad (\gamma = \text{const.} \neq 0), \tag{38}$$

$$A = B\eta,^{13} \tag{39}$$

on peut former une expression explicite du u présentant la solution d'un problème particulier où les données initiales ne sont plus indépendantes, mais liées par une certaine relation.

[13] Dans cette égalité η est une fonction convenablement choisie.

§ 5

Supposons maintenant que la fonction u déterminée par la formule (35), remplit encore la condition aux limites:

$$u_{x=0} = ln\,[1 + \epsilon(t)], \tag{40}$$

où

$$|\,\epsilon(t)\,| < \delta < 1.$$

La formule (35) nous donne:

$$\frac{2}{\kappa\theta(0,t)}\left[e^{\int_a^{at}\frac{\Omega}{H}d\zeta}\pm\frac{\sqrt{\Omega^2(at)+4}}{H(at)}+e^{\int_a^{at}\frac{\Omega(at)}{H(at)}}\right]$$

$$\times\left[e^{\int_a^{-at}\frac{\Omega}{H}d\zeta}\pm\frac{\sqrt{\Omega^2(-at)+4}}{H(-at)}-e^{\int_a^{-at}\frac{\Omega}{H}d\zeta}\frac{\Omega(-at)}{H(-at)}\right]$$

$$=[1+\epsilon(t)]^{\kappa}\left[\int_0^{at}e^{\int_a^{\lambda}\frac{\Omega}{H}d\zeta}\pm\frac{\sqrt{\Omega^2+4}}{H}d\lambda+e^{\int_a^{at}\frac{\Omega}{H}d\zeta}\right.$$

$$\left.-\left(\int_a^{-at}e^{\int_a^{\lambda}\frac{\Omega}{H}d\zeta}\pm\frac{\sqrt{\Omega^2+4}}{H}d\lambda-e^{\int_a^{-at}\frac{\Omega}{H}d\zeta}\right)\right]^2. \tag{41}$$

En posant:

$$at=z;\quad t=\frac{z}{a},$$

$$e^{\int_a^{z}\frac{\Omega}{H}d\zeta}=K(z), \tag{42 a}$$

$$\int_0^{z}e^{\int_a^{\lambda}\frac{\Omega}{H}d\zeta}\pm\frac{\sqrt{\Omega^2+4}}{H}ds$$

$$=\pm\int_0^{z}\frac{K(\lambda)\sqrt{\Omega^2+4}}{H}d\lambda=\Delta(z), \tag{42 b}$$

on trouve:

$$\frac{2}{\kappa\theta\left(0, \frac{z}{a}\right)} [\Delta'(z) + \mathrm{K}'(z)] [\Delta'(-z) - \mathrm{K}'(-z)]$$

$$= \left[1 + \epsilon\left(\frac{z}{a}\right)\right]^{\kappa} [\Delta(z) - \Delta(-z) + \mathrm{K}(z) + \mathrm{K}(-z)]^2. \tag{43}$$

Il est évident que l'équation (31) détermine une liaison fonctionnelle entre Ω et les fonctions θ, H, ψ. L'équation (43) constitue une autre liaison entre ces élements et la fonction ϵ.

Remarque.—Dans quelques cas particuliers la relation (43) peut être remplacée par une formule plus simple.

Supposons que Ω est une fonction *impaire*. Dans ce cas H et ψ, comme le fait voir l'équation (31), doivent être des *fonctions paires*.

En admettant cette hypothèse on peut écrire:

$$\mathrm{K}(z) = \overline{\mathrm{K}}(z) = \overline{\mathrm{K}}(-z),$$

$$\overline{\mathrm{K}}'(z) = -\overline{\mathrm{K}}'(-z),$$

$$\Delta'(z) = \overline{\Delta}'(z) = \overline{\Delta}'(-z),$$

$$\overline{\Delta}(z) = \mathrm{I}(z) + \mathrm{C}'^{14}$$

$$\overline{\Delta}(z) - \overline{\Delta}(-z) = 2\mathrm{I}(z);$$

$$\frac{1}{2\kappa\theta\left(0, \frac{z}{a}\right)} [\mathrm{I}'(z) + \mathrm{K}'(z)]^2 = \left[1 + \epsilon\left(\frac{z}{a}\right)^{\kappa} \cdot [\mathrm{I}(z) + \overline{\mathrm{K}}(z)]^2; \tag{44}$$

en posant ensuite:

$$\mathrm{I}(z) + \overline{\mathrm{K}}(z) = \Lambda(z), \tag{45}$$

il vient:

$$\Lambda'(z) \mp \sqrt{2\kappa\theta\left(0, \frac{z}{a}\right)\left[1 + \epsilon\left(\frac{z}{a}\right)\right]^{\kappa}}\, \Lambda(z) = 0 \tag{46}$$

[14] Je dèsigne par I (z) une fonction impaire.

$$\Lambda(z) = C'' e^{\pm \int_a^z \sqrt{2\kappa\theta\left(0, \frac{\lambda}{a}\right)\left[1+\epsilon\left(\frac{\lambda}{a}\right)\right]^\kappa}\, d\lambda}. \tag{47}$$

En tenant compte des égalités (42 *a*), (42 *b*). (45) on a:

$$e^{\int_a^z \frac{\Omega}{H} d\zeta} = \frac{\Lambda'(z)\, H(z)}{\pm\sqrt{\Omega^2(z)+4}+\Omega(z)}.$$

$$\frac{\Omega}{H} = \frac{\Lambda''}{\Lambda'} + \frac{H'}{H} - \frac{\Omega'}{\pm\sqrt{\Omega^2+4}}.$$

En éliminant Ω' de cette dernière égalité, à l'aide de (31) et en posant, pour abréger:

$$\frac{\Lambda''}{\Lambda'} + \frac{H'}{H} \mp \psi = \frac{\Lambda''}{\Lambda'} + \frac{H'}{H} - \frac{\Psi}{2} = \delta. \tag{48}$$

on trouve:

$$\Omega = \frac{H\delta}{2} - \frac{2}{H\delta}. \tag{49}$$

La transformation effectuée sera admissible, si la fonction Ω, donnée par l'égalité (49), présente réellement une fonction impaire. Cette condition, ainsi que le résultat trouvé par la substitution de l'expression (49) au lieu de Ω dans l'équation (31) auront pour conséquence une certaine relation entre θ, H, Ψ ou, ce qui revient au même,—entre θ, F et G.

Signalons, encore, en terminant cette analyse provisoire, une condition *suffisante*, sous laquelle la fonction u, satisfaisant à (40), remplit encore la condition aux limites:

$$u_{x=l} = ln\,[1 + \epsilon(t)]. \tag{50}$$

On voit aisément que la condition (50) sera identique à la condition (40), si les fonctions Ω, H, $\int_a^z \Omega/H\, d\zeta$ et Δ admettent la période et si, au surplus, a lieu la relation:

$$\theta(l, t) = \theta(0, t).$$

§ 6

Considérons une méthode particuliére permettant de former les solutions des équations (11), (14) qui satisfont aux conditions aux limites sans prescrire d' avance à ces solutions les valeurs initiales. (Une étude pareille peut avoir une raison d'être à cause des complications auxquelles nous a mené la méthode du § 5).[15]

Cherchons donc une solution de (11) ou (14) remplissant les conditions (40) et (50).

En tenant compte des formules (12), (40) et des désignations (18) et en posant $at = z$, on a:

$$A'(z)\,B'(-z) = \frac{\kappa}{2}\,\theta\left(0, \frac{z}{a}\right)\left[1 + \epsilon\left(\frac{z}{a}\right)\right]^{\kappa}\,[A(z) - B(-z)]^2; \tag{51 a}$$

d'une manière analogue, on trouve, à l'aide de (12), (50):

$$A'(l+z)\,B'(l-z) = \frac{\kappa}{2}\,\theta\left(l, \frac{z}{a}\right)\left[1 - \epsilon\left(\frac{z}{a}\right)\right]^{\kappa} \times [A(l+z) - B(l-z)]^2. \tag{51 b}$$

En introduisant des nouvelles fonctions arbitraires M, N, λ par les égalités:

$$A(z) = -\,M(z)\,\lambda(z), \tag{52 a}$$

$$B(z) = N(-z)\,\lambda(-z) \tag{52 b}$$

et en substituant ces valeurs dans (51 *a*) on recoit, pour déterminer λ, l'équation différentielle:

$$\left(M' + M\frac{\lambda'}{\lambda}\right)\left(N' + N\frac{\lambda'}{\lambda}\right) = \frac{\kappa}{2}\,\theta\left(0, \frac{z}{a}\right)\left[1 + \epsilon\left(\frac{z}{a}\right)\right]^{\kappa}(M+N)^2. \tag{53}$$

---

[15] Une solution du problème étudié remplissant à la fois les conditions de Cauchy et les conditions aux limites peut être trouvée à l'aide d'une série convenablement choisie représentant R; la formation d'une telle série sera l'objet d'un mémoire que j'ai déjà entrepris et que j'espére avoir encore le temps de terminer.

En posant:

$$\frac{\kappa}{2}\,\theta\left(0,\frac{z}{a}\right)\left[1+\epsilon\left(\frac{z}{a}\right)\right]^{\kappa}=\mathrm{S}(z) \tag{54}$$

et en désignant par ϵ une constante arbitraire, il viendra:

$$\lambda(z)=\frac{E}{\sqrt{\mathrm{M}(z)\,\mathrm{N}(z)}}$$

$$\times\, e^{\pm\frac{1}{2}\int_{\tau}^{z}\left\{\sqrt{\left[\frac{\mathrm{M}'(\zeta)}{\mathrm{M}(\zeta)}-\frac{\mathrm{N}'(\zeta)}{\mathrm{N}(\zeta)}\right]^{2}+4\mathrm{S}(\zeta)\left[\frac{\mathrm{M}(\zeta)}{\mathrm{N}(\zeta)}+\frac{\mathrm{N}(\zeta)}{\mathrm{M}(\zeta)}+2\right]}\right\}d\zeta}$$

$$=\frac{E}{\sqrt{\mathrm{M}(z)\,\mathrm{N}(z)}}\,e^{\pm\frac{1}{2}\mathrm{T}(z)}. \tag{55}$$

Ainsi on peut écrire:

$$\mathrm{A}(z)=-E\sqrt{\frac{\mathrm{M}(z)}{\mathrm{N}(z)}}\,e^{\pm\frac{1}{2}\mathrm{T}(z)}, \tag{56 a}$$

$$\mathrm{B}(z)=+E\sqrt{\frac{\mathrm{N}(-z)}{\mathrm{M}(-z)}}\,e^{\pm\frac{1}{2}\mathrm{T}(-z)}. \tag{56 b}$$

En transformant (51 b) à l'aide de (52 a), 52 b), il vient:

$$[\mathrm{M}'(l+z)\,\lambda(l+z)+\mathrm{M}(l+z)\,\lambda'(l+z)]\,[\mathrm{N}'(z-l)\,\lambda(z-l$$

$$+\mathrm{N}(z-l)\,\lambda'(z-l)]$$

$$=\frac{\kappa}{2}\,\theta\left(l,\frac{z}{a}\right)\left[1+\epsilon\left(\frac{z}{a}\right)\right]^{\kappa}[\mathrm{M}(l+z)\,\lambda(l+z)$$

$$+\mathrm{N}(z-l)\,\lambda(z-l)]^{2}. \tag{57}$$

Cherchons les conditions *suffisantes* sous lesquelles l'équation (57) devient identique à l'équation (53).

Supposons (*I*) —Les fonctions M, N, identifier les équations fonctionnelles:

$$\mathrm{M}(z+l)=\frac{1}{\omega}\,\mathrm{M}(z), \tag{58 a}$$

$$\mathrm{N}(z+l) = \frac{1}{\omega}\,\mathrm{N}(z).^{16} \qquad (58\,b)$$

Il est alors aisé de former une équation fonctionnelle de la même forme pour la fonction λ.

On trouve:

$$\lambda(z+l) = \frac{E\omega}{\sqrt{\mathrm{M}(z)\,\mathrm{N}(z)}}\, e^{\pm i\mathrm{T}(z+l)}.$$

Supposons maintenant encore (II) que:

$$\mathrm{S}(z+l) = \theta\left(0, \frac{z+l}{a}\right)\left[1+\epsilon\left(\frac{z+l}{a}\right)\right]^{\varkappa}$$

$$= \theta\left(0, \frac{z}{a}\right)\left[1+\epsilon\left(\frac{z}{a}\right)\right]^{\varkappa} = \mathrm{S}(z); \qquad (59)$$

en tenant compte de la signification du symbole $\mathrm{T}(z)$ on peut alors écrire:

$$\mathrm{T}'(z+l) = \mathrm{T}(z)$$

$$\mathrm{T}(z+l) = \mathrm{T}(z) + \gamma,$$

où γ désigne une constante.

L'équation cherchée peut donc être exprimée par la formule:

$$\lambda(z+l) = \omega e^{\pm i\gamma}\,\lambda(z). \qquad (60)$$

Prenant en considération les égalités (58 *a*), (58 *b*), (60), on réduit l'équation (57) à la forme suivante:

$$\left(\mathrm{M}' + \mathrm{M}\frac{\lambda'}{\lambda}\right)\left(\mathrm{N}' + \mathrm{N}\frac{\lambda'}{\lambda}\right)$$

$$= \frac{\varkappa}{2}\,\theta\left(l, \frac{z}{a}\right)\left[1+\epsilon\left(\frac{z}{a}\right)\right]^{\varkappa}(\mathrm{M}e^{\pm i\gamma} + \mathrm{N}e^{+i\gamma})^2. \qquad (61)$$

En identifiant cette équation avec l'équation (53) il faut distinguer deux cas:

(1) $\gamma \neq 0$ (*III'*)

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[16] Ici w est une constante quelconque. On pourrait introduire dans les équations (58 *a*), (58 *b*), au lieu de cette constante, une fonction $w(z)$, mais une transformation pareille ne changerait pas les resultats de la discussion et ne nous conduirait pas aux généralisations utiles.

En considérant le système (53), (61) on trouve la relation:

$$(\mathrm{M}e^{\pm\frac{1}{2}\gamma} + \mathrm{N}e^{\pm\frac{1}{2}\gamma})^2\,\theta\left(l, \frac{z}{a}\right) - (\mathrm{M} + \mathrm{N})^2\,\theta\left(0, \frac{z}{a}\right) = 0, \tag{62}$$

qui nous donne la formule:

$$\mathrm{M} = (-1)^{m+n}\,\frac{\sqrt{\theta\left(0, \frac{z}{a}\right)} + (-1)^{m-1}\,e^{\frac{(-1)^{\tau-1}\gamma}{2}}\sqrt{\theta\left(l, \frac{z}{a}\right)}}{e^{\frac{(-1)^{\tau}\gamma}{2}}\sqrt{\theta\left(l, \frac{z}{a}\right)} + (-1)^{m-1}\sqrt{\theta\left(0, \frac{z}{a}\right)}}\,\mathrm{N} = \xi(z)\mathrm{N}.^{17} \tag{63}$$

En introduisant les solutions:

$$\mathrm{M}(z) = \omega^{-z/e}\,\Pi_1(z), \tag{64 a}$$

$$\mathrm{N}(z) = \omega^{-z/e}\,\Pi_2(z),^{18} \tag{64 b}$$

des équations fonctionnelles (58 *a*), (58 *b*) nous constatons que la fonction ξ doit admettre la période 1; pour remplir cette condition *il suffira de supposer* (*IV'*) *que*:

$$\theta\left(0, \frac{z+l}{a}\right) = \theta\left(0, \frac{z}{a}\right)^{19} \tag{65 a}$$

$$\theta\left(l, \frac{z+l}{a}\right) = \theta\left(l, \frac{z}{a}\right). \tag{65 b}$$

On trouve ensuite:

$$\mathrm{A}(z) = -\,E\sqrt{\xi(z)}\,e^{\pm\frac{1}{2}\mathrm{T}(z)}$$

$$\mathrm{B}(z) = +\,E\sqrt{\frac{1}{\xi(-z)}}\,e^{\pm\frac{1}{2}\mathrm{T}(z)},$$

$$\mathrm{T}(z) = \int_{\tau}^{z} \{\sqrt{\xi'^2(\zeta) + 4\mathrm{S}(\zeta)\,\xi(\zeta)\,[\xi(\zeta)+1]^2}\}\,\frac{d\zeta}{\xi(\zeta)} \tag{66}$$

---

[17] Les radicaux dans cette formule sont écrit comme radicaux arithmétiques car leur multiformité est prise en considération dans les exposants *m*, *n*, qui affectent les unités negatives.

[18] Par π_1, π_2 sont désignés les fonctions arbitraires admettant la période *l*.

[19] Les équations (65 *a*), (59) ont pour conséquence la périodicité de la fonction E.

Pour pouvoir satisfaire à la relation (60) nous devons, évidemment, *faire encore la supposition* (V')[20]: *l'équation*:

$$\int_0^l \{\sqrt{\xi'^2(\zeta) + 4S(\zeta)\,\xi(\zeta)\,[\xi(\zeta) + 1]^2}\}\,\frac{d\zeta}{\xi(\zeta)} = \gamma \tag{67}$$

doit admettre une solution γ *réelle et différente de zéro.*

Remarque.—Signalons un cas particulier intéressant.

Soit:

$$\theta\left(l, \frac{z}{\alpha}\right) = \theta\left(0, \frac{z}{\alpha}\right),\ m + n = 2s;$$

de cette relation on déduit:

$$\xi(z) = e^{\mp\frac{\gamma}{2}},$$

$$A(z) = -Ee^{\mp\frac{\gamma}{4} \pm \frac{1}{2}T(z)},$$

$$B(z) = +Ee^{\pm\frac{\gamma}{4}\pm\frac{1}{2}T(-z)}$$

$$T(z) = 2\left(e^{\pm\frac{\gamma}{4}} + e^{\mp\frac{\gamma}{4}}\right)\int_\tau^z [\sqrt{S(\zeta)}]\,d\zeta. \tag{68}$$

La condition (V') se réduira à l'existence d'une racine γ, réelle et différante de zéro, de l'équation:

$$2\left(e^{\pm\frac{\gamma}{4}} + e^{\mp\frac{\gamma}{4}}\right)\int_0^l [\sqrt{S(\zeta)}]\,d\zeta = \gamma. \tag{69}$$

Il est aisé de voir qu' une solution pareille existera toujours, quand la valeur de l'intégrale est suffisamment petite.

La fonction u, satisfaisante aux conditions aux limites (40), (50) et calculée en supposant valables les postulats (I), (II), (III'), (IV'), est exprimée par la formule:

[20] Du reste, équivalente à la condition (III').

$$u = \frac{1}{k}\{- ln2 - lnk \pm \tfrac{1}{2}[\mathrm{T}(at + x) + (at - x)]\}$$

$$+ ln\{[\pm \xi(at + x)\,\mathrm{T}'(at + x)] + \xi'(at + x)]$$

$$\times [\pm \xi(at - x)\,\mathrm{T}'(at - x) - \xi'(at - x)]\}$$

$$- \tfrac{1}{2} ln[\xi(\cdot t + x)\,\xi(at + x)] - ln\theta(x, t)$$

$$- 2ln[\sqrt{\xi(at + x)\,\xi(at - x)}\; e^{\pm\frac{1}{2}\mathrm{T}(at+x)} + e^{\pm\frac{1}{2}\mathrm{T}(at-x)}]\}. \tag{70}$$

Il est aisé d'écrire les valeurs initiales de cette solution. On trouve:

$$u_{t=0} = \mathrm{F}(x) = \frac{1}{k}\{- ln2 - lnk \pm \tfrac{1}{2}[\mathrm{T}(x) + \mathrm{T}(-x)]$$

$$+ ln\{[\pm \xi(x)\,\mathrm{T}'(x) + \xi'(x)]\,[\pm \xi(-x)\,\mathrm{T}'(-x)$$

$$- \xi'(-x)]\} - \tfrac{1}{2} ln[\xi(x)\,\xi(-x)] - ln\theta(x, 0)$$

$$- 2ln[\sqrt{\xi(x)\,\xi(-x)}\; e^{\pm\frac{1}{2}\mathrm{T}(x)} + e^{\pm\frac{1}{2}\mathrm{T}(-x)}]\} \tag{71 a}$$

$$\left(\frac{\partial u}{\partial t}\right)_{t=0} = \mathrm{G}(x)$$

$$= \frac{a}{\kappa}\left\{\frac{2\xi(x)\,\xi''(x) - \xi'^2(x) + \xi^2(x)\,\mathrm{T}'(x)^2 \pm 2[\xi^2(x)\,\mathrm{T}''(x) + \xi(x)\,\xi'(x)\,\mathrm{T}'(x)]}{2\xi(x)\,[\xi'(x) \pm \xi(x)\,\mathrm{T}'(x)]}\right.$$

$$- \frac{\xi^2(-x)\,\mathrm{T}'^2(-x) - 2\xi(-x)\,\xi''(-x) + 3\xi'^2(-x) \pm 2[\xi^2(-x)\,\mathrm{T}''(-x) - \xi(-x)\,\xi'(-x)\,\mathrm{T}'(-}{2\xi(-x)\,[\xi'(-x) \mp \xi(-x)\,\mathrm{T}'(-x)]}$$

$$- \frac{e^{\pm\frac{1}{2}\mathrm{T}(x)}\,[\xi'(x) \pm \xi(x)\,\mathrm{T}'(x)]\,\sqrt{[\xi(x)]^3} - e^{\pm\frac{1}{2}\mathrm{T}(-x)}\,[\xi'(-x) \mp \xi(-x)\,\mathrm{T}'(-x)]\,\sqrt{\xi(x)}}{\xi(-x)\,\sqrt{\xi(x)}\,[\sqrt{\xi(x)\,\xi(-x)}\; e^{\pm\frac{1}{2}\mathrm{T}(x)} + e^{\pm\frac{1}{2}\mathrm{T}(-x)}]}$$

$$\left. - \frac{1}{a\theta(x, 0)}\left[\frac{\partial\theta(x, t)}{\partial t}\right]_{t=0}\right. \tag{7}$$

Nous avons formé la solution d'un problème particulier, où les valeurs initiales dépendent du facteur θ.

(2) *Soit maintenant* $\gamma = 0$ (*III″*).—En supposant valables les conditions (I), (II), (III″), on voit que l'équation (61) devient identique à l'équation (53), *si* (*IV″*):

$$\theta\left(l, \frac{z}{a}\right) = \theta\left(0, \frac{z}{a}\right). \tag{72}$$

Dans le cas étudié la fonction $T'(z)$ doit être la dérivée d'une fonction admettant la période l. En formant $T'(z)$ à l'aide de (64 *a*), (67 *b*), il viendra:

$$T'(z) = \sqrt{4S(z)\left[\frac{\Pi_1(z)}{\Pi_2(z)} + \frac{\Pi_2(z)}{\Pi_1(z)} + 2\right] - \left[\frac{\Pi_1(z)}{\Pi_2(z)}\right]^1 \cdot \left[\frac{\Pi_2(z)}{\Pi_1(z)}\right]^1}$$

De cette formule, en posant pour abréger:

$$\frac{\Pi_1(z)}{\Pi_2(z)} = \Pi(z),$$

on trouve:

$$T'(z) = \frac{1}{\Pi(z)} \sqrt{[\Pi'(z)]^2 + 4S(z)\Pi(z)[\Pi(z) + 1]^2}. \tag{73}$$

Il est clair que pour satisfaire à la condition (III″) il faut et il suffit de *supposer* (*V″*) *l'existence de l'égalité*:

$$\int_0^l \{\sqrt{[\Pi'(\zeta)]^2 + 4S(\zeta)\Pi(\zeta)[\Pi(\zeta) + 1]}\}^2 \frac{d\zeta}{\Pi(\zeta)} = 0. \tag{74}$$

Prenant en considération qu'en vertu de (64 *a*), (64 *b*):

$$M(z) = \Pi(z)\, N(z) \tag{75}$$

on voit que dans le cas étudié on peut obtenir les expressions de u, $u_{t=0}$ $(\partial u/\partial t)_{t=0}$ en remplacant, respectivement, dans les formules (70), (71 *a*), (71 *b*) fonction ξ par la fonction Π. Comme cette dernière fonction, hormis la périodicité, doit seulement satisfaire à la relation, (74) on conclut que, dans le cas considéré, une des deux valeurs initiales peut être fixée, pour ainsi dire, presque arbitrairement; la seconde valeur sera calculée comme une grandeur dépendante de la première.

§ 7

Considérons, pour terminer, quelques exemples.

1. Discutons le cas d'une force stabilisante ($\theta = -1$), caractérisée par les formules (7) et (8) et par la condition accessoire:

$$w_{t=0} = f(x), \tag{76}$$

et supposons que

$$A_1(s) = A_2(s) = Q(s).$$

Les formules (8) et (76) nous donnent:

$$w = \frac{1}{k}\left\{2ln2 \pm \sqrt{2\kappa}\left[\int_{\tau}^{s+at} e^{\frac{\kappa f(\zeta)}{2}} d\zeta + \int_{\tau}^{s-at} e^{\frac{\kappa f(\zeta)}{2}} d\zeta\right]\right.$$

$$+ \frac{k}{2}\left[f(x+at) + f(x-at)\right] +$$

$$\left. - 2ln\left[e^{\pm\sqrt{2\kappa}\int_{\tau}^{s+at} e^{\kappa f(\zeta)/2} d\zeta} + e^{\pm\sqrt{2\kappa}\int_{\tau}^{s-at} e^{\kappa f(\zeta)/2} d\zeta}\right]\right\} \quad (77)$$

$$\left(\frac{\partial w}{\partial t}\right)_{t=0} = 0. \quad (78)$$

Nous avons trouvé la solution explicite d'un problème de Cauchy, déterminée par les équations (7), (76), (78).

2. Considérons un exemple du calcul de la solution de l'équation (11), satisfaisante aux conditions (40) et (50).

Soient:

$$E(t) = 0,$$

$$S(z) = \frac{\kappa}{2}\,\theta\left(l, \frac{z}{a}\right) = \frac{\kappa}{2}\,\theta\left(0, \frac{z}{a}\right) = \frac{\kappa}{2}\left(\epsilon + \rho\,\cos\frac{2\pi z}{l}\right)^2;$$

en posant encore $\kappa = \frac{1}{2}$, $v = 1$, $l = 1$, on écrira l'équation (69) sous la forme:

$$e^{\gamma/4} + e^{-\gamma/4} = \gamma.$$

Nous choisirons pour γ, la plus petite des deux racines de cette équation:

$$\gamma = \gamma_1 \cong 2{,}3576.$$

En posant encore $\tau = 0$, la formule (68) nous donne:

$$T(z) = \gamma_1\left(z + \frac{\rho}{2\pi}\sin 2\pi z\right),$$

$$T'(z) = \gamma_1 (1 + \rho \cos 2\pi z).$$

Soit enfin:

$$\theta(x, t) = (1 + \rho \cos 2\pi a t)^2 - \rho^2 \sin^2 2\pi x.$$

En tenant compte de tout cela, on trouve:

$$\xi(z) = e^{-\gamma_1/2}.^{21}$$

$$u = 4 ln \gamma_1 - \gamma_1 + \frac{\rho \gamma_1}{\pi} \sin 2\pi a t \cos 2\pi x$$

$$+ ln \left[\frac{(1 + \rho \cos 2\pi a t \cos 2\pi x)^2 - \rho^2 \sin^2 2\pi x t \sin^2 2\pi x}{(1 + \rho \cos 2\pi a t) - \rho^2 \sin^2 2\pi x} \right]^2$$

$$- ln \left\{ e^{-\frac{\gamma_1}{2} + \frac{\gamma_1}{2} \left[x + \frac{\rho}{2\pi} \sin 2\pi (at + X) \right]} \right.$$

$$\left. + e^{\frac{\gamma_1}{2} \left[-x + \frac{\rho}{2\pi} \sin 2\pi (at - X) \right]} \right\}^4 \tag{79}$$

Cette solution satisfait aux conditions aux limites:

$$u_{x=0} = u_{x=1} = 0$$

et aux conditions de Cauchy:

$$u_{t=0} = ln \left\{ \frac{\gamma_1 (1 + \rho \cos 2\pi x)}{2 \left[\sqrt{(1 + \rho)^2 - \rho^2 \sin^2 2\pi x} \right] \operatorname{ch} \left[\frac{\gamma_1}{2} \left(x + \frac{\rho}{2\pi} \sin 2\pi x \right) - \frac{\gamma_1}{4} \right]} \right\}^4, \tag{80}$$

$$\left(\frac{\partial u}{\partial t} \right)_{t=0} = 0. \tag{81}$$

Les formules (79), (80) seront valables pour toutes les valeurs réelles de x, t, sous la restriction $|\rho| < \frac{1}{2}$.

La formule (79) détermine le mouvement d'une corde de longueur 1 ayant ses extrémités fixes sous l'influence de forces perturbatrices suivantes:

[21] Nous choisissons partout le supérieur des deux signes $\pm$ ou $\mp$.

(1) de la force égale à:

$$4a^2e^{u/2}\,[(1+\rho\cos 2\pi at)^2-\rho^2\sin^2 2\pi x]$$

pour chaque unité de la masse et résultante d'une force perturbatrice d'un champ électromagnétigue homogène et variable, et d'une force stabilisante d'un champ électromagnétique continu hétérogène;

(2) de la force indépendante, de u et résultante de deux forces, égales, respectivement, pour chaque unité de la masse à:

$$-2\frac{\delta^2 ln\theta}{\partial t^2}=8\pi^2a^2\rho\left[\frac{\rho+(1+\rho\sin 2\pi x)\cos 2\pi at}{(1+\rho\cos 2\pi at+\rho\sin 2\pi x)^2}\right.$$

$$\left.+\frac{\rho+(1-\rho\sin 2\pi x)\cos 2\pi at}{(1+\rho\cos 2\pi at-\rho\sin 2\pi x)^2}\right]$$

et à

$$2a^2\frac{\partial^2 ln\theta}{\partial x^2}=-8\pi^2a^2\rho\left[\frac{(1+\rho\cos 2\pi at)\sin 2\pi x+\rho}{(1+\rho\cos 2\pi at+\rho\sin 2\pi x)^2}+\right.$$

$$\left.-\frac{(1+\rho\cos 2\pi at)\sin 2\pi x-\rho}{(1+\pi\cos 2\pi at-\rho\sin 2\pi x)^2}\right].$$

Le mouvement est périodique.

3. 'Etudions un exemple de l'application de la formule (15).

Posons:

$$\theta(x,t)=[1+\rho\cos 2\pi(x+at)]^2,\quad l=1,\quad k=\tfrac{1}{2},\quad \epsilon(t)=0.$$

Les expressions de S (z), T (z), T′ (z) et la valeur de γ_1 seront les mêmes que dans l'exemple 2.

Nous recevons les formules:

$$u=4ln\gamma_1-\gamma_1+\frac{\rho\gamma_1}{\pi}\sin 2\pi at\,\cos 2\pi x$$

$$+ln\left\{\frac{[(1+\rho\cos 2\pi at\cos 2\pi x)^2-\rho^2\sin^2 2\pi at\sin^2 2\pi x]^2}{(1+\rho\cos 2\pi(x+at))^4}\right\}$$

$$-ln\left\{e^{\frac{-a_1}{2}+\frac{a_1}{2}\left[x+\frac{\rho}{2\pi}\sin 2\pi(x+at)\right]}\right.$$

$$+ e^{\frac{\alpha_1}{2}\left[-a+\frac{\rho}{2\pi}\sin 2\pi\,(at-x)\right]^4}\Bigg\}; \tag{82}$$

$$u_{t=0} = ln\left\{\frac{\gamma_1}{2ch\left[\frac{\gamma_1}{2}\left(x+\frac{\rho}{2\pi}\sin 2\pi x\right)-\frac{\gamma_1}{4}\right]}\right\}^4; \tag{83}$$

$$\left(\frac{\delta u}{\delta t}\right)_{t=0} = \frac{8a\pi\rho\sin 2\pi x}{1+\rho\cos 2\pi x}. \tag{84}$$

Nous avons trouvé la solution d'*un probléme de Ramàn-Dey*, caractérisé par l'équation:

$$\frac{\delta^2 u}{\delta t^2} - a^2\frac{\delta^2 u}{\delta X^2} = 4a^2\,[1+\rho\cos 2\pi\,(x+at)]^2\,e^{u/2}$$

et les valeurs initiales (83), (84); cette solution satisfait aux conditions:

$$u_{X=0} = 0, \qquad u_{X=1} = 0.$$

Le mouvement est périodique; il est borné sous la restriction $|\rho| < \frac{1}{2}$.

4. Considérons enfin un exemple de la résolution de l'équation (14) avec les conditions accessoires (40), (50), $\epsilon(t) = 0$, $\gamma = 0$.

Soient:

$$\Pi(z) = \mathrm{P} = +\text{ const.};$$

$$\theta(x,t) = \mathrm{M}(at+x)\,\mathrm{M}(at-x);$$

il vient alors:

$$\mathrm{S}(z) = \frac{\kappa}{2}\,\mathrm{M}^2(z).$$

Posons encore:

$$\mathrm{M}(z) = \sum_{m=1}^{\infty}\left(a_m\cos\frac{2m\pi z}{l} + b_m\sin\frac{2m\pi z}{l}\right),$$

la série dans le second membre étant supposée uniformément convergente avec ses dérivées du premier et du second ordre.

On trouve:

$$T'(\zeta) = \frac{1}{\Pi(\zeta)} \sqrt{[\Pi'(\zeta)]^2 + 4S(\zeta)\Pi(\zeta)[\Pi(\zeta)+1]^2}$$

$$= (P+1)\sqrt{\frac{\kappa}{2P}} \sum_{m=1}^{\infty} \left(a_m \cos \frac{2m\pi\zeta}{l} + b_m \sin \frac{2m\pi\zeta}{l} \right).$$

Il est clair que dans notre exemple:

$$\int_0^1 \left\{ \sqrt{[\Pi'(\zeta)]^2 + 4S(\zeta)\Pi(\zeta)[\Pi(\zeta)+1]^2} \frac{d\zeta}{\Pi(\zeta)} = 0 \right\};$$

les conditions (I), (II), (III″), (IV″) sont évidemment satisfaites.

La fonction u est déterminée par la formule:

$$u = \frac{1}{\kappa} ln \left\{ \frac{(P+1)^2}{4P ch^2 \left[1 ln P \pm \frac{(P+1)\,l}{2\pi} \sqrt{\frac{\kappa}{2P}} \sum_{m=1}^{\infty} \frac{\sin \frac{2m\pi x}{l}}{m} \left(a_m \cos \frac{2m\pi at}{l} + b_m \sin \frac{2m\pi at}{l} \right) \right]} \right\} \tag{85}$$

Les valeurs initiales sont données par les égalités:

$$u_{t=0} = \frac{1}{\kappa} ln \left\{ \frac{(P+1)^2}{4P ch^2 \left[\frac{1}{2} ln P \pm \frac{(P+1)\,l}{2\pi} \sqrt{\frac{\kappa}{2P}} \sum_{m=1}^{\infty} \frac{a_m}{m} \sin \frac{2m\pi x}{l} \right]} \right\}, \tag{86}$$

$$\left(\frac{\partial u}{\partial t} \right)_{t=0} = \mp 2d(P+1) \sqrt{\frac{\kappa}{2P}} \left(\sum_{m=1}^{\infty} b_m \sin \frac{2m\pi x}{l} \right)$$

$$\times th \left[1 ln P \pm \frac{(P+1)\,l}{2\pi} \sqrt{\frac{\kappa}{2P}} \sum_{m=1}^{\infty} \frac{a_m}{m} \sin \frac{2m\pi x}{l} \right]. \tag{87}$$

La formule (85) nous donne la solution *du problème de Ramàn-Dey* caractérisé par l'équation:

$$\frac{\partial^2 u}{\partial t^2} - a^2 \frac{\partial^2 u}{\partial x^2}$$

$$= 4a^2 \left\{ \sum_{m=1}^{\infty} \left[a_m \cos \frac{2m\pi (at + x)}{l} + b_m \sin \frac{2m\pi (at + x)}{l} \right] \right\}$$

$$\times \left\{ \sum_{m=1}^{\infty} \left[a_m \cos \frac{2m\pi (at - x)}{l} + b_m \sin \frac{2m\pi (at - x)}{l} \right] \right\} l^{\kappa u}$$

et les conditions (86), 87), (40), (50). Cette solution est bornée et admet la période l/a. Les valeurs initiales renferment une constante arbitraire P.

RECIPROCAL LATTICE PHOTOGRAPHY

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1. Introduction

Of the single-crystal X-ray photographic methods, the method of reciprocal lattice photography yields undistorted records of the reciprocal lattice. The photographs obtained are not only symmetry-true but also enable one to index the spots by visual inspection.

The well-known De-Jong Bouman camera was the first of its kind. Improved types of cameras were later designed and constructed by M. J. Buerger. A publication bearing the title "The Photography of the Reciprocal Lattice" by M. J. Buerger published as a A.S.X.R.E.D. Monograph, No. 1, 1944 gives in detail the principles involved in reciprocal lattice photography and describes a reciprocal camera, its uses, and advantages over other methods. The principle involved can be stated very briefly as follows: The Ewald construction for the reflection of X-rays by a set of planes indicates that an X-ray reflection occurs whenever a reciprocal lattice point intersects the sphere of reflection. The direction of the reflected beam is got by joining the centre of the reflecting circle and the reciprocal lattice point. If one can always keep the film plane parallel to the reciprocal lattice plane that is being investigated, the record obtained under such conditions represents a scaled replica of the reciprocal lattice plane. This can be shown to be the case with a simple geometric construction shown in Fig. 1. In order to cover as many points of the reciprocal plane as is convenient, a very ingenious kind of rotation has been introduced, in which the normals to the reciprocal lattice plane and the film plane follow a motion, similar to that of a precessing top about an axis which is the direction of the incident X-ray beam. Hence the instrument was given the name "X-ray precession camera". An arrangement is provided in the camera for this type of precessional motion wherein it is possible to set different angles of precession. In order that the film and the reciprocal lattice should remain parallel to each other during the motion, a link system is incorporated in the design of the camera. Further, a layer-line screen whose distance can be altered with

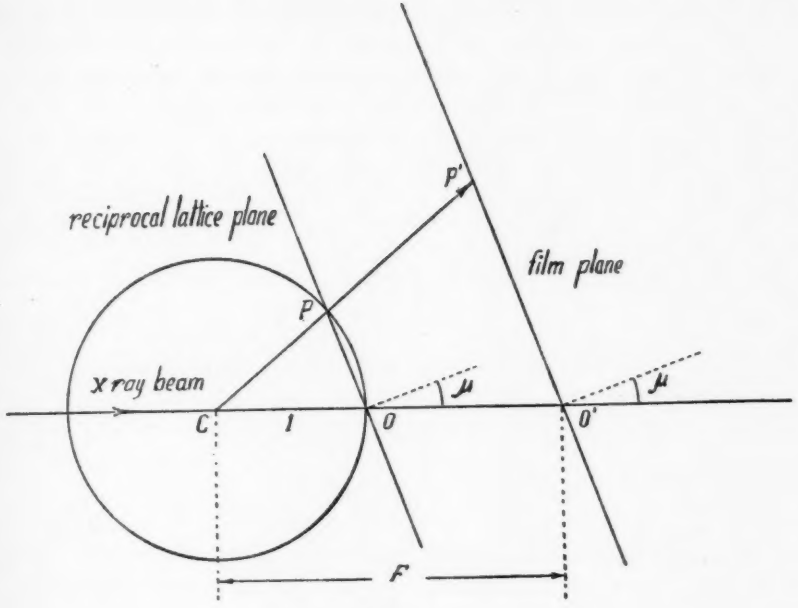

FIG. 1

$$\frac{O'P'}{OP} = \frac{CO'}{CO} = \frac{F}{1} \quad \therefore O'P' = F.OP$$

respect to the crystal is provided, with a view to isolate reflections of a particular layer. A movement for translating the film towards the crystal is also provided so that different reciprocal planes can be recorded without distortion. The geometric conditions necessary for obtaining these results are described and discussed in detail in the book referred to above.

The construction of such a camera was undertaken at this Institute and the present communication describes the same. It is not claimed that the instrument incorporates any new features. It appeared worthwhile however to describe our experience in making and using such a camera for the benefit of those interested in such work.

2. THE CONSTRUCTIONAL FEATURES

A photograph of the reciprocal camera is reproduced in Fig. 2. The different parts of the camera described in this section can be clearly seen on an inspection of the same. The arc-shaped arm which is the principal part of the driving mechanism of the camera can be seen. The arc was cut out

of ¼″ brass plate and represents a part of a circle of radius 16·5 cm., the segment subtending an angle of about 40° at the centre. It is mounted on a bush bearing which is supported on a pillar fixed to the base. The arm can be rotated by a motor about the X-ray beam as its axis. A sliding block on the arm carries the driving axis which goes and fits into a cylindrical brass bush attached to the back of the film holder carrier. The sliding piece at its lowest setting represents a precession angle of 0°, while at the maximum it represents a precession angle of 30°. A square frame which carries the film holder is mounted on a two-axis universal joint. The unmoved point of the universal joint is precisely set in the centre of the circle mentioned above. A sliding arrangement is provided for translating the film holder towards the crystal. The crystal holder assembly is mounted on another two-axis universal joint. The distance between the film and the crystal universal joint centres represents the specimen to film distance, which has been set at 6 cm. in the instrument. The crystal holder assembly supports an L-shaped arm, and this carries a movable layer-line screen. The layer-line screen is made out of brass sheet, 10 cm. square, with an annular opening of 15 mm. in radius. A layer-line screen with an annular opening of 30 mm. in radius will also be found useful. Provision has therefore been made to be able to use the desired layer-line screen. A parellelogram link motion with ball and socket joints at the upper two corners serves as the link between the reciprocal lattice plane and the film plane. The precessional motion executed by the latter is transmitted by this link to the former, maintaining at the same time both the planes strictly parallel. The link is attached at its two lower ends to the projecting horizontal, film and crystal axes. For facilitating initial setting of the crystal, the link at the crystal axis end can be decoupled, leaving the crystal axis free. Further, the platforms which support the film holder carrier and the crystal holder are coupled by two brass links. This serves as a parallelogram link in the horizontal plane. The former link has to be of the ball and socket type, since it has to take care of parallelogram motions in two mutually perpendicular planes. The latter link is absolutely necessary, but is of a very simple type as it has to take care of a parallelogram motion in one plane only, namely, the horizontal plane. The X-ray collimator is carried by the pillar which is seen at the extreme left of the photograph. There is a lead stop which serves to screen off the incident beam after it has emerged from the crystal.

The universal joint carrying the film holder is capable of being moved along the axis of the instrument, while the universal joint carrying the crystal is capable of being moved at right angles to this axis. The X-ray collimator can similarly be moved at right angles to the axis of the instrument. After

proper alignment, these can be firmly clamped. The geometry of the instrument strictly demands that the incident X-ray beam should pass through the two universal joint centres which remain unmoved during the motion. The beam should be set parallel to the axis of the instrument.

In making these universal joints, a tapered cone assembly was used for the vertical axis. Very smooth and satisfactory running is ensured by putting a steel ball on top of the male cone, such that the hollow cone part rests on the steel ball, at the same time remaining just in contact with the male cone. This arrangement helps in reducing the grip between the two members which would otherwise result, and has been found to be very satisfactory. For the horizontal axis two ball bearings were used. A major portion of the instrument was made by machining $\frac{1}{2}''$ thick perspex sheet. It is very easy to shape this material and stick pieces of these together with trichloroethylene. Wherever necessary, pieces were stuck and strengthened by screws and nuts. Since the instrument was at the outset started as a model, the above materials were used, but to our surprise, the materials have been found to be very satisfactory.

Smooth running of the instrument depends on accurate alignment and accurate balancing of the different parts. It may not be out of place to mention here that the camera can be made at a cost much less than one has to pay for the commercially available ones.

3. Photography by the Precession Method

A preliminary step in recording reciprocal lattice photographs is to set the chosen axis of the crystal, parallel to the X-ray beam. If the axis of the crystal is roughly set by trial photographs, or from its known optical properties, accurate setting can be made by taking a series of precession photographs at small precession angles. Such photographs can be taken with short exposure times. The procedure for setting is explained in the book referred to. Once the axis is set parallel to the X-ray beam, the instrument is ready for recording the reciprocal lattice. For recording the zero layer, the film is kept such that its centre coincides with the unmoved point of the universal joint through which the X-ray beam also passes and intersects the film normally. The desired precession angle is then set. The appropriate layer-line screen is chosen and its distance from the crystal is set according to the equation

$$r_s/S = \tan \cos^{-1} (\cos \mu - d^*)$$

where r_s is the radius of the annular opening, S is the screen to crystal distance, μ is the precession angle and d^* is the reciprocal lattice spacing. For

zero layer, d^* is zero and the equation reduces to $r_s/S = \tan \mu$. For recording of higher planes, the appropriate value of d^* should be substituted in the equation.

For recording n levels without distortion, it is necessary to displace the film away from the universal joint centre towards the crystal, by a distance:

$$d' = Fd^*$$

where F is the crystal to film distance, and d^* the reciprocal lattice plane spacing.

Three X-ray precession photographs are reproduced in the plate accompanying this paper. Fig. 3 is a zero layer reciprocal lattice photograph of quartz recorded with the trigonal axis as the precession axis. Mo white radiation was employed. Fig. 4 is again a zero layer photograph of quartz taken with MoKα radiation. Fig. 5 represents the zero layer reciprocal lattice photograph recorded with the b-axis, of the monoclinic crystal cobalt nitrate hexahydrate, as the precession axis. In this case MoKα radiation was used.

The chief advantages of the method are, that it gives a scaled replica of the reciprocal lattice and indexing can be carried out by visual inspection. With crystals of large spacing, the determination of the space-group is comparatively quicker. Another advantage is that if a crystal is set with one crystallographic axis parallel to the goniometer axis, information regarding two reciprocal cell-axes can be obtained without having to remount the crystal, as in the case of other methods. After obtaining photographs about one axis, one has to rotate the crystal through the appropriate angle to bring the second reciprocal cell-axis along the X-ray beam to obtain the records. This is decidedly a great advantage over other methods and especially so when one is dealing with crystals of small dimensions and in low temperature X-ray crystallography.

The author wishes to express his grateful thanks to Professor Sir C. V. Raman, F.R.S., N.L., for his interest in the work. It is a pleasure to thank Dr. S. Ramaseshan for the many illuminating discussions the author had with him.

SUMMARY

A precession X-ray camera constructed at this Institute is described. Reciprocal lattice photographs of quartz and $CO(NO_3)_2\,6H_2O$ recorded with the camera are reproduced and the general principles involved in X-ray reciprocal lattice photography are discussed.

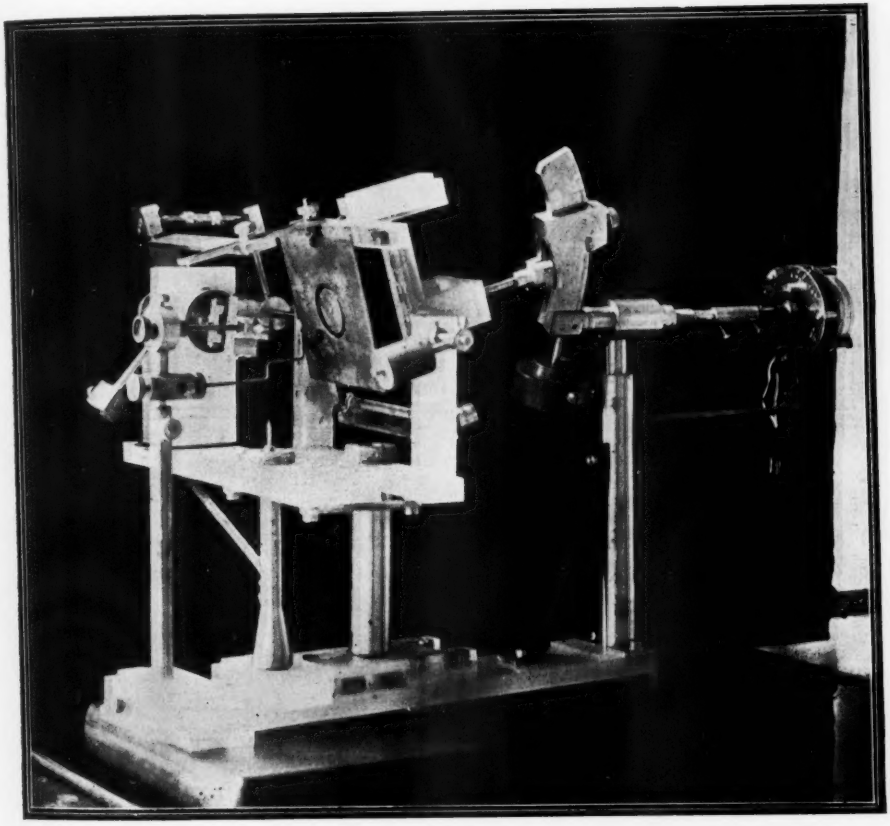

FIG. 2

FIG. 3

FIG. 4

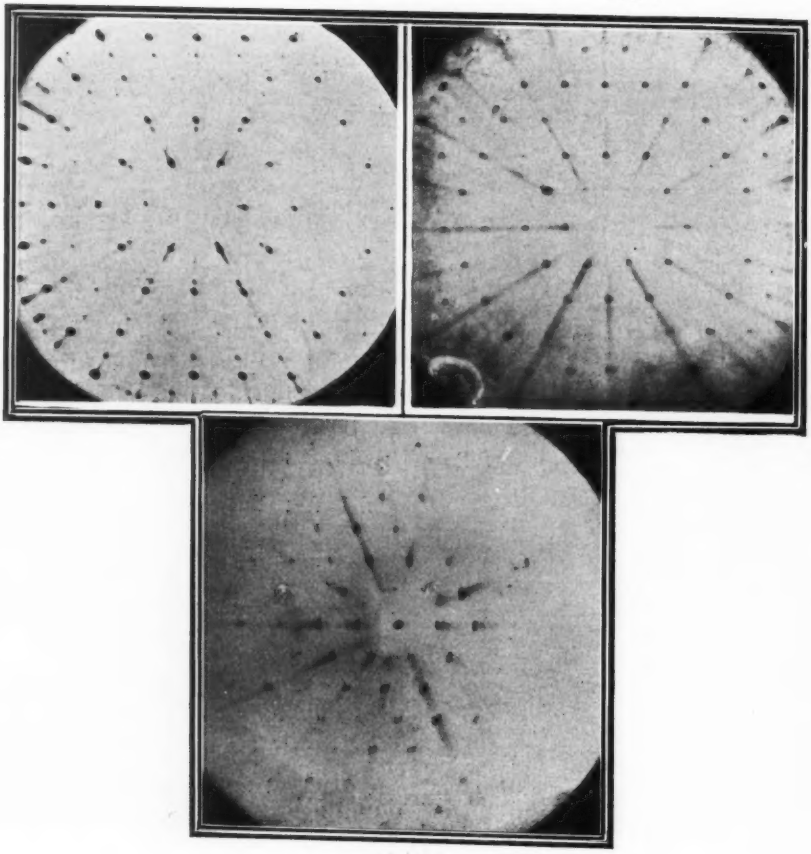

FIG. 5

UNIT CELL PARAMETERS, SPACE-GROUP AND OPTICAL PROPERTIES OF COBALT NITRATE HEXAHYDRATE

By A. Jayaraman

(*Memoir No.* 106 *from the Raman Research Institute, Bangalore-6*)

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Cobalt nitrate hexahydrate crystallises from aqueous solution as large platy crystals which are highly deliquescent. According to Groth the crystal belongs to the monoclinic system with axial ratios $a:b:c::1\cdot172:1:1\cdot925$ and $\beta = 101°$. The density is given as $1\cdot88$ gm./c.c. In a previous paper in these *Proceedings* (1957, **45,** 263), the unit cell parameters and optical properties of nickel nitrate hexahydrate were reported. In the same connection it was thought worthwhile to investigate the structure and optical properties of cobalt nitrate hexahydrate. In the present communication the unit cell parameters, space-group and optical properties of the crystal are reported.

Cobalt nitrate hyxahydrate was crystallised by making a saturated solution and allowing the same to crystallise in an air-tight enclosure containing anhydrous calcium chloride in a dish. Large platy crystals reddish orange in colour were obtained in this manner, which were dried between filter-papers and kept immersed in kerosene. Examination of one of the plates under the polarising microscope exhibited straight extinction. The crystal was mounted on the Federov stage, with kerosene as the immersion medium and rotated about the straight extinction edge as the axis. The crystal continued to remain extinguished and exhibited a biaxial figure when examined in convergent polarised light.

For X-ray work, a thin rod-shaped piece ground parallel to the straight extinction edge was employed, and this was enclosed in a thin-walled glass capillary tube sealed at one end and blocked at the other with wax. Since the crystal is highly deliquescent, it had to be protected from attack by moisture during X-ray exposure in the above manner.

One rotation, and three Weissenberg photographs were taken with the crystal rotated about the axis chosen, employing NiKα radiation. The three

Weissenberg photographs were respectively, the zero, first and second layer photographs. A perusal of the rotation and zero layer Weissenberg photographs revealed that the axis of rotation was the *b*-axis of a crystal belonging to the monoclinic system. One more rotation and zero layer Weissenberg photograph was recorded rotating the crystal about another crystallographic axis, perpendicular to the *b*-axis. Axial dimensions were calculated from rotation and Weissenberg photographs and are as follows:

$$a = 15{\cdot}09 \text{ AU}$$

$$b = 6{\cdot}12 \text{ AU} \qquad \beta = 119°$$

$$c = 12{\cdot}69 \text{ AU}$$

From the measured density of 1·9 and the calculated volume on the basis of the above dimensions, the number of molecules per unit cell turns out to be 4.

The Weissenberg photographs were indexed and the following conditions for the presence of reflections were noted.

$$hkl : h + k = 2n$$

$$hol : l = 2n \; ; (h = 2n)$$

$$oko : k = 2n$$

On looking up the *International Tables*, the monoclinic space-groups C/*c* and C2/*c* satisfy these conditions. Of these two, C/*c* has no centre of symmetry. Optical examination did not reveal the presence of optical activity, the brush crossing the eye being quite definitely dark. It is highly probable that the crystal belongs to the monoclinic space-group C2/*c*. Complete structure determination is under progress.

Optical Properties

The convergent light figure is observed on the habit plane which corresponds to the $(\bar{1}01)$ face of the crystal, when referred to the axes chosen on the basis of the X-ray results. The principal vibration direction parallel to the *b*-crystallographic axis is found to be the intermediate or β index of refraction. The orientation of the optical elements are shown in Fig. 1.

The refractive indices for sodium light were measured by employing the immersion method with a polarising microscope and an universal stage. The values determined are as follows:

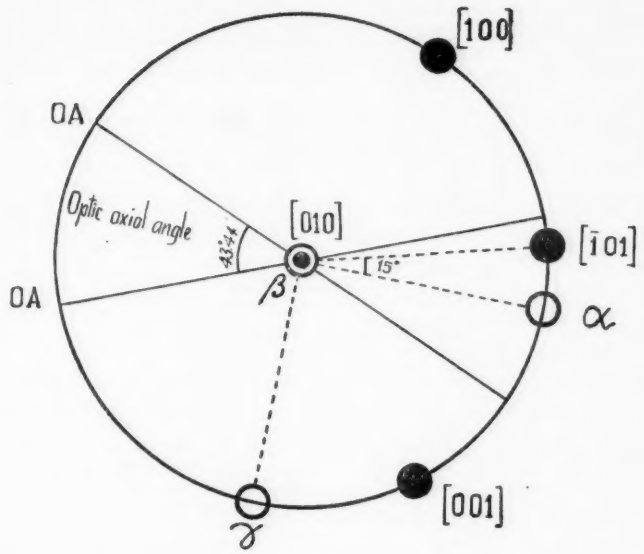

FIG. 1

$\alpha = 1{\cdot}38$

$\beta = 1{\cdot}52$ $\quad 2V = 43° 44'$

$\gamma = 1{\cdot}547$

The crystal is biaxial negative.

Pleochroism is not marked for the vibration direction parallel to β and γ. But for a vibration parallel to α and γ the effect is very vivid. For the former the colour is purple and for the latter it is orange yellow.

The author in conclusion wishes to express his thanks to Professor Sir C. V. Raman for his interest in the investigation.

THE EMISSION SPECTRUM OF IODINE BROMIDE EXCITED IN THE PRESENCE OF ARGON

Part I. The Band System in the Regions 5425–5360 Å, 4520–4415 Å and 4120–4010 Å

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Received October 5, 1957

ABSTRACT

IBr vapour was excited in the presence of argon by an uncondensed transformer discharge. Four band systems were obtained in the regions 5425–5360 Å, 4520–4415 Å, 4120–4010 Å and 3915–3540 Å of which the first three are discussed in this paper. The wavelengths and wavenumbers of the band heads in three systems as measured from the plates obtained with a 3-prism Steinheil glass spectrograph are given along with their visually estimated relative intensities. The three band systems, which are new, are analysed and the following vibrational constants expressed in cm.$^{-1}$ are obtained:

Band system	ν_e	ω_e''	$\omega_e''x_e''$	$\omega_e''y_e''$	ω_e'	$\omega_e'x_e'$
5425–5360 Å	18613	65·5	0·24	−0·01	43·0	0·026
4520–4415 Å	22312	65·5	0·24	−0·01	77·0	0·5
4120–4010 Å	24540	160·6	1·125	..	128·4	0·1

The lower state of the first two systems has been identified with the (O^+) state at 16814 cm.$^{-1}$ reported earlier by Brown from a study of the absorption bands in the visible region.

INTRODUCTION

ASUNDI and Venkateswarlu[1] excited IBr vapour by an uncondensed transformer discharge and recorded a number of continuous bands in the region 5200–2300 Å some of which correspond to some fluorescence bands obtained

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earlier by Filippov.[2] Haranath and Rao,[3] by exciting IBr vapour with a condensed transformer discharge reported recently about 40 bands in the region 3900–3800 Å and explained them as due to a transition from an upper state at 38306 cm.$^{-1}$ to the lower state at 12230 cm.$^{-1}$, established earlier by Brown[4] from a study of absorption in the near infrared region. They also obtained some bands in the region 1975–1740 Å, which were reported to correspond to those obtained by Cordes and Sponer[5] in absorption.

Iodine, bromine and chlorine are known[6] to give groups of diffuse bands or continua when excited without the presence of a foreign gas. But when they are excited in the presence of a foreign gas, they give new discrete band systems. Filippov[2] could not detect any such discrete band system by exciting IBr vapour in the presence of N_2. This is probably because the pressure of N_2 used by him might not have been high enough and also because the dispersion of the spectrograph used was very small. As the results that had been obtained in this laboratory by exciting I_2, Br_2 and Cl_2* in the presence of argon were encouraging, the problem of studying the spectrum of IBr excited under similar conditions has been taken up and the results obtained in the region 6000–4000 Å are discussed in this paper.

Experimental Results

Iodine bromide was excited in the presence of argon with an uncondensed transformer discharge and the spectrum obtained was photographed with a 3-prism Steinheil glass spectrograph with long camera and a Hilger E_1 Littrow quartz spectrograph. The other experimental details are similar to those described earlier in the case of bromine.[7] As the pressure of argon is increased the continuous bands that one gets by exciting the IBr vapour without the presence of argon, slowly disappear and a new spectrum results. The new spectrum consists of short band systems in the regions (1) 5425–5360 Å, (2) 4520–4415 Å and (3) 4120–4010 Å together with an extensive band system in the region 3915–3540 Å. Besides these systems, the 2950–2670 Å band system of Br_2 and the 4400–4000 Å and 3450–3015 Å band systems of I_2 discussed in the earlier papers[7, 8] are also detected. The band systems of I_2 appear, however, more strongly than that of Br_2. It was found that by the introduction of fresh samples of IBr vapour at frequent intervals the intensity of the I_2 band systems could be considerably decreased and of IBr systems enhanced.

Figure 1 shows the spectrum obtained by exciting IBr vapour in the presence of argon as photographed with a Hilger E_1 Littrow quartz spectro-

* Recent work that is in progress in this laboratory shows that Cl_2 excited in the presence of argon shows a discrete band system in the region 2600–2400 Å.

graph in the region 4800–3350 Å. The spectrum of I_2 obtained under similar conditions in the same region is also shown for comparison. Bromine excited in the presence of argon does not show any band system in this region. The band system 5425–5360 Å, 4520–4415 Å and 3915–3540 Å can easily be attributed to IBr because I_2 and Br_2 excited under similar conditions do not show any discrete band systems in these regions. The 4120–4010 Å band system is sometimes overlapped by the weak bands of the 4400–4000 Å system of I_2 whose strong part lies in the region 4300–4200 Å. But by introducing fresh samples of IBr vapour at frequent intervals and by adjusting the time of exposure it is possible to photograph the spectrum in such a way that the I_2 bands are visible in the region 4300–4200 Å, and not in the region 4120–4010 Å so that the 4120–4010 Å system of IBr is obtained without any trace of I_2 bands.

THE BAND SYSTEMS IN THE REGIONS 5425–5360 Å AND 4520–4415 Å

The 5425–5360 Å system.—Figure 2 shows the enlargement of the spectrum in the region 5425–5360 Å obtained with a 3-prism Steinheil glass spectrograph. The bands are degraded to longer wavelengths. The wavelengths and wavenumbers of the band heads are listed in Table I along with

TABLE I

Wavelengths, wavenumbers and relative intensities of the bands in the system 5425–5360 Å

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
1	5422·1	18438	3	5393·0	18537
1	5420·0	18451	3	5387·6	18556
2	5413·1	18469	6	5381·4	18577
2	5409·9	18480	2	5378·7	18587
2	5405·1	18496	8	5373·8	18604
2	5399·2	18516	2	5369·8	18618
2	5397·5	18522	8	5362·6	18643

their visually estimated relative intensities. The measurements were made from the plates taken with the 3-prism Steinheil glass spectrograph. The error in the measurements of band heads may be $\pm$ 2 cm.$^{-1}$ The vibrational

analysis of the bands is shown in Table II. The bands fall in sequences, the strongest of which is represented as the $\Delta v = 0$ sequence.

TABLE II

The vibrational scheme for the bands in the system 5425–5360 *Å*

v'' / v'	0	1	2	3	4	$\Delta G'(v+\frac{1}{2})$ Obs.	$\Delta G'(v+\frac{1}{2})$ Cal.
0	18604	18537	18469				
	67	68					
	39	40	47			42·0	43·0
1	18643	18577	18516	18451			
	66	61	65				
		41	40	45		42·0	42·9
2		18618	18556	18496	18438		
		62	60	58			
			48	41	42	43·7	42·9
3			18604	18537	18480		
			67	57			
			39	50	42	43·7	42·8
4			18643	18587	18522		
			56	65			
$\Delta G''(v+\frac{1}{2})$ Obs.		66·5	63·6	62·0	60·0		
$\Delta G''(v+\frac{1}{2})$ Cal.		65·0	64·5	63·9	63·2		

The 4520–4415 Å system.—The enlargement of the spectrum in the region 4520–4415 Å obtained with a 3-prism Steinheil glass spectrograph is shown in Fig. 3. The degradation of the bands in general is not clear, though some of the bands appear to be degraded to longer wavelengths and a few to the shorter wavelengths. The wavelengths and wavenumbers of band heads as obtained from the plates taken on the 3-prism Steinheil glass spectrograph are tabulated in Table III along with their visually estimated relative intensities. The vibrational analysis of the bands is given in Table IV. The error in measurements of band heads may be $\pm$ 3 cm.$^{-1}$ The bands of this system like those of the 5425–5360 Å system fall mainly in sequences and the sequence starting with the strongest bands is represented as the $\Delta v = 0$ sequence.

The $\Delta G''(v + \frac{1}{2})$ values obtained for the 5425–5360 Å system are quite close to those obtained for the 4520–4415 Å system which suggests that the

TABLE III

Wavelengths, wavenumbers and relative intensities of the bands in the system 4520–4415 *Å*

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
2	4518·9	22123	3	4458·8	22421
2	4510·3	22165	3	4455·6	22437
2	4505·8	22187	3	4450·0	22466
2	4502·7	22203	3	4447·6	22478
2	4493·4	22249	3	4446·4	22484
5	4490·1	22265	6	4445·1	22490
6	4488·0	22275	6	4443·3	22500
8	4484·5	22293	2	4440·7	22513
8	4482·2	22304	2	4438·4	22524
10	4479·0	22320	4	4437·2	22530
10	4478·2	22324	5	4435·8	22538
5	4475·1	22340	2	4432·6	22554
5	4471·1	22360	1	4431·2	22561
1	4468·4	22373	0	4430·5	22565
1	4466·0	22385	1	4424·8	22594
1	4464·4	22393	0	4422·6	22605
1	4463·4	22398	0	4415·1	22643

two systems have a common lower state. It is quite likely that the lower state of these two systems is the (O^+) state at 16880 cm.$^{-1}$ reported by Brown[4] from the study of the visible absroption bands. The $\triangle G(v+\frac{1}{2})$ values obtained by Brown for this state from $v=8$ to $v=37$ are plotted against v along with the $\triangle G''(v+\frac{1}{2})$ values of the 4520–4415 Å system from $v=0$ to $v=7$. The $\triangle G''(v+\frac{1}{2})$ values of the system 5425–5360 Å from $v=0$ to $v=3$ are also plotted in the same graph (see Fig. 4). It was found that within the experimental error all the points plotted can be fairly represented by a smooth curve and all the $\triangle G(v+\frac{1}{2})$ values can be expressed by the vibrational constants $\omega_0 = 65{\cdot}3$ cm.$^{-1}$, $\omega_0 x_0 = 0{\cdot}23$ cm.$^{-1}$ and $\omega_0 y_0 = 0{\cdot}01$ cm.$^{-1}$ The calculated and observed $\triangle G''(v+\frac{1}{2})$ are given in Tables II and IV for comparison. All the bands of the 5425–5360 Å system can be

TABLE IV

The vibrational scheme for the bands in the system 4520–4415 Å

v' \ v''	0	1	2	3	4	5	6	7	8	$\Delta G'$ $(v+\frac{1}{2})$ Obs.	$\Delta G'$ $(v+\frac{1}{2})$ Cal.
0	22320	22249	22187	22123							
	71	62	64								
	73	75	78	80						76·5	76·0
1	22393	22324	22265	22203							
	69	59	62								
	73	75	72							73·5	75·0
2	22466	..	22340	22275							
			65								
	72									72·0	74·0
3	22538	22478	..	..	22293	..	22165				
	60										
		76								71·5	73·0
4		22554	22484	22421	22360	22304	..				
		70	63	61	56						
		77	69	77	69					73·0	72·0
5			22561	22490	22437	22373	22304	22249			
			71	53	64	69	55				
			75	63	64	81	71			70·8	71·0
6				22565	22500	22437	22385	22320	22265		
				65	63	52	65	55			
					76			73		74·5	70·0
7					..	22513	..	22393	..		
										..	69·0
8					22643	..	22524	..	22398		
										..	68·0
9								22530	..		
								64		64·0	67·0
10								22594	22538		
									56		
									67	67·0	66·0
11									22605		
$\Delta G''$ $(v+\frac{1}{2})$ Obs.	66·7	63·7	65·0	59·7	61·0	60·5	60·0	55·5			
$\Delta G''$ $(v+\frac{1}{2})$ Cal.	65·0	64·5	63·9	63·2	62·5	61·7	60·9	60·1			

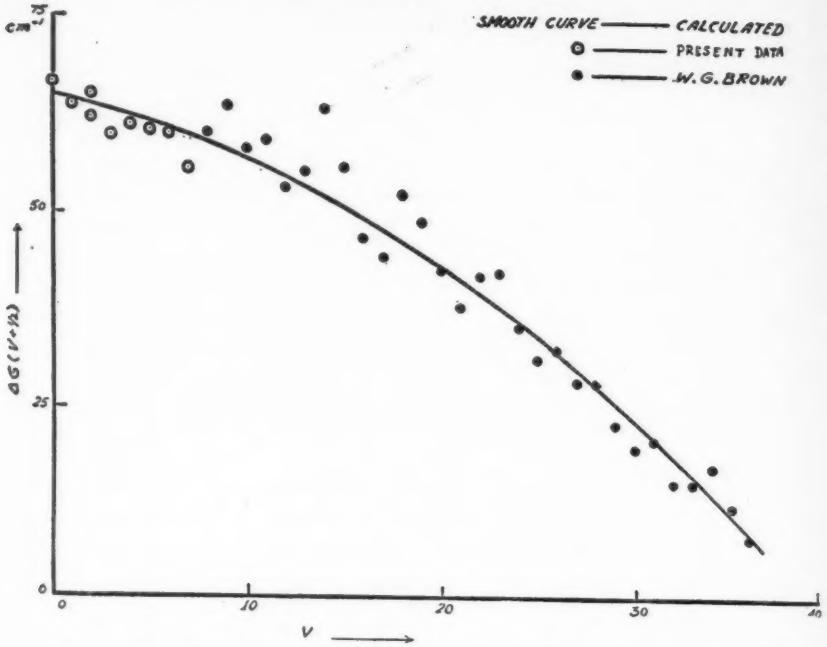

FIG. 4. The graph showing the $\Delta G(v + \frac{1}{2})$ *versus* v of (O^+) state at $T_e = 16814$ cm.$^{-1}$

fairly well represented by the formula $v = 18602 + (43{\cdot}0\,v' - 0{\cdot}026\,v'^2) - (65{\cdot}3\,v'' - 0{\cdot}23\,v''^2 - 0{\cdot}01\,v''^3)$ and similarly those of the 4520–4415 Å system can be represented by the equation

$$\nu = 22318 + (76{\cdot}5\,v' - 0{\cdot}5\,v'^2) - (65{\cdot}3\,v'' - 0{\cdot}23\,v''^2 - 0{\cdot}01\,v''^3)$$

As the lowest level of the (O^+) state observed by Brown is $v = 8$, he obtained $T_e = 16880$ cm.$^{-1}$ of the state by extrapolation from $v = 8$ to $v = 0$ assuming that the $\Delta G(v + \frac{1}{2})$ remains constant as 60 cm.$^{-1}$ for those levels. It is not necessary now to use such an extrapolation, since the $\Delta G''(v + \frac{1}{2})$ values from $v = 0$ to $v = 7$ are observed in the present experiments. Using the vibrational constants obtained from the present work and taking into consideration the experimental data of Brown regarding the position of the level $v = 8$, the ω_e and T_e for the state (O^+) are obtained to be 65·5 cm.$^{-1}$ and 16814 cm.$^{-1}$ respectively.*

* According to Brown's observation the position of the level $v = 8$ of the (O^+) state above the $v = 1$ of the ground state, is at 16947·8 cm.[1] Using $\omega_0 = 267{\cdot}6$ cm.$^{-1}$ for the ground state, the position of the level $v = 8$ of the (O^+) state above the level $v = 0$ of the ground state, is at 17214·6 cm.$^{-1}$ The height of the level $v = 8$ over the level $v = 0$ of the (O^+) state as obtained from the vibrational constants, $\omega_0 = 65{\cdot}3$ cm.$^{-1}$, $\omega_0 l_0 = 0{\cdot}23$ cm.$^{-1}$ and $\omega_0 y_0 = 0{\cdot}01$ cm.$^{-1}$ is 502·6 cm.$^{-1}$ This gives $T_e = 16712$ cm.$^{-1}$ from which T_e can be calculated as 16814 cm.$^{-1}$

Thus the position of the upper level of the 5425–5360 Å system is at $T_e = 35427$ cm.$^{-1}$ and that of the 4520–4415 Å system is $T_e = 39126$ cm.$^{-1}$

The Band System in the Region 4120–4010 Å

Figure 5 shows the enlargement of the spectrum in the region 4120–4010 Å taken with 3-prism Steinheil glass spectrograph. The spectrum consists of bands degraded to longer wavelengths and also bands degraded to shorter wavelengths. The wavelengths and wavenumbers of band heads obtained from the plates taken with a 3-prism Steinheil glass spectrograph are given in Table V along with their visually estimated relative intensities.

Table V

Wavelengths, wavenumbers and relative intensities of the bands in the system 4120–4010 Å

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
1	4117·8	24278	6	4062·4	24609
2	4104·9	24355	4	4060·5	24621
3	4099·3	24387	3	4059·4	24627
3	4096·9	24402	4	4058·4	24633
8	4091·1	24437	2	4055·5	24651
8	4086·5	24464	5	4055·0	24654
4	4084·0	24479	2	4050·7	24680
5	4082·8	24486	3	4048·7	24692
8	4081·4	24495	0	4047·6	24699
10	4076·2	24526	1	4045·8	24710
10	4073·5	24542	1	4043·3	24725
8	4071·0	24557	2	4043·0	24727
10	4069·8	24564	1	4041·2	24738
3	4069·3	24567	0	4040·2	24744
2	4068·0	24575	1	4035·3	24774
4	4066·2	24586	1	4034·5	24779
7	4065·2	24592	1	4027·5	24822
4	4063·4	24603	1	4015·2	24898
			1	4014·1	24905

The error in measurements of band heads may be $\pm 1 \cdot 5$ cm.$^{-1}$ The Deslandres scheme of the bands degraded to longer wavelengths is shown in Table VI. The bands fall in sequences, the strongest of which is represented as the $\triangle v = 0$ sequence and the strongest band as the (0, 0) band. All the bands can fairly well be represented by the formula $\nu = 24524 + (128 \cdot 3\, v' - 0 \cdot 1\, v'^2) - (159\,45\, v'' - 1 \cdot 125\, v''^2)$ with $v' = 0 - 5$ and $v'' = 0 - 4$.

TABLE VI

The vibrational scheme for the bands degraded to longer wavelengths in the system 4120–4010 Å

v'' / v'	0	1	2	3	4	$\triangle G'$ $(v+\frac{1}{2})$ Obs.	$\triangle G'$ $(v+\frac{1}{2})$ Cal.
0	24526						
	128					128·0	128·0
1	24654	24495					
	159						
	125	126				125·5	127·8
2	24779	24621	24464				
	158	157					
	126		128			127·0	127·6
3	24905	..	24592	24437			
			155				
				127		127·0	127·4
4				24564			
						..	127·2
5					24542		
$\triangle G''$ $(v+\frac{1}{2})$ Obs.	158·5	157·0	155·0	..			
$\triangle G''$ $(v+\frac{1}{2})$ Cal.	158·2	155·8	153·4	151·0			

The Deslandres scheme for the bands degraded to shorter wavelengths is shown in Table VII where n' and n'' are arbitrary. These bands also fall in sequences. It was found that these bands can also be represented by the same formula as that for the bands in Table VI with $n' = 19$ and $n'' = 17$. Therefore it seems likely that the bands of Table VII may be the tail bands of those shown in Table VI.

TABLE VII

The vibrational scheme for the bands degraded to shorter wavelengths in the system 4120–4010 Å

TABLE VII

The vibrational scheme for the bands degraded to shorter wavelengths in the system 4120–4010 Å

v' \ v''	$n''+0$	$n''+1$	$n''+2$	$n''+3$	$n''+4$	$n''+5$	$n''+6$	$n''+7$	$n''+8$	$n''+9$	$n''+10$	$n''+11$	$n''+12$	$n''+13$	$n''+14$	$\Delta G''$ Cal. $(v+\frac{1}{2})$	$\Delta G''$ $(v+\frac{1}{2})$ Obs.
$n'+0$ ..	24567																
	125															125·0	124·4
$n'+1$ ..	24692	24575	..	24355													
	117																
	124			124												124·0	124·2
$n'+2$ ..	24699	24586	24479														
	113	107															
	123	124	124													123·7	124·0
$n'+3$ ..	24822	24710	24603	24486	..	24278											
	112	107	117														
		122	123		124											122·0	123·8
$n'+4$ ..		24725	24609	..	24402												
		116															123·6
			129													129·0	
$n'+5$ ..			24738	24627	*	*											123·4
			111													..	
$n'+6$ ..						*	24567										123·2
							125									125·0	
$n'+7$ ..							24692	*									123·0
																..	
$n'+8$ ..									24710	*							
																..	122·8
$n'+9$ ..										24744	24651	24557	..	24387			
											93	94					
											123	123				123·0	122·6
$n'+10$ ..											24774	24680	..	..			
												94					
											124					124·0	122·4
$n'+11$.											24898	..	24633	..			
$\Delta G''$ $(v+\frac{1}{2})$ Obs.	117·0	112·5	107·0	116·5	111·0	..	..	..	..	..	93·0	94·0	..	..			
$\Delta G''$ $(v+\frac{1}{2})$ Cal.	116·9	114·4	112·0	109·5	107·1	104·6	102·2	99·7	97·3	94·8	92·4	90·0	87·6	85·1			

Note:—The bands expected for the positions marked (*) in the above table are overlapped by the strong bands degraded to longer wavelengths falling at the same positions.

It may be mentioned that it was not possible to identify any of the two states involved in the 4120–4010 Å system with any of the known levels of the IBr molecule.

The authors take this opportunity to express their sincere thanks to Prof. R. K. Asundi for the permission to use the 3-prism Steinheil glass spectrograph in the Department of Spectroscopy, Hindu University, Benaras. Thanks are also due to the U.P. Government Research Committee for financial assistance.

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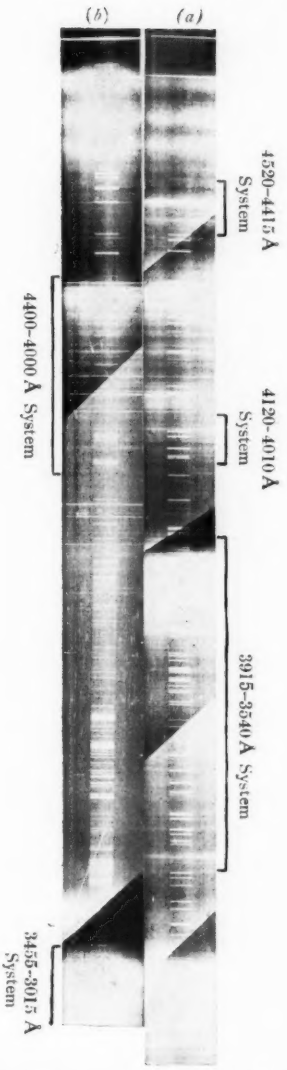

FIG. 1. (*a*) Enlargement of the spectrum of IBr excited in the presence of argon taken with Hilger E_1 Littrow quartz spectrograph in the region 4800–3350 Å.

(*b*) Enlargement of the spectrum of I_2 excited in the presence of argon taken with Hilger E_1 Littrow quartz stpectrograph in the region 4800–3350 Å.

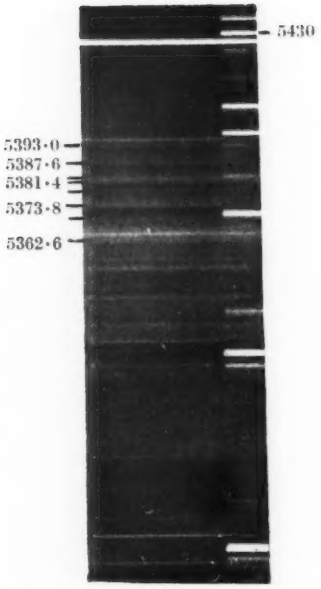

FIG. 2. Enlargement of the spectrum of IBr excited in the presence of argon taken with 3-prism Steinheil glass spectrograph in the region 5425–5360 Å.

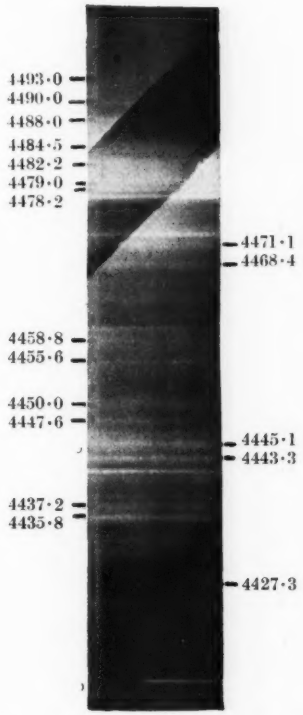

FIG. 3. Enlargement of the spectrum of IBr excited in the presence of argon taken with 3-prism Steinheil glass spectrograph in the region 4520–4415 Å.

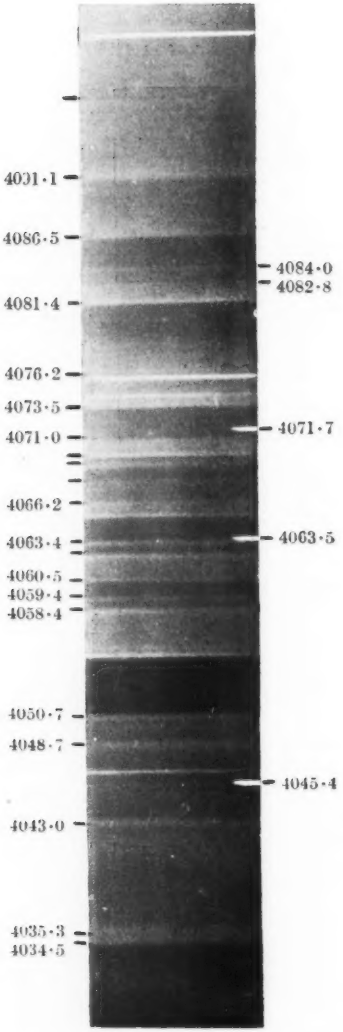

FIG. 5. Enlargement of the spectrum of IBr excited in the presence of argon taken with 3-prism Steinheil glass spectrograph in the region 4120–4010 Å.

THE EMISSION SPECTRUM OF IBr EXCITED IN THE PRESENCE OF ARGON

Part II. The Band System in the Region 3915-3540 Å

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ABSTRACT

Wavelengths and wavenumbers of the band heads in the region 3915–3540 Å are recorded as obtained from the measurements of the plates taken on a first order 21-feet grating spectrograph. Earlier workers recently reported 40 bands of this system covering the region 3900–3800 Å. All the bands of this system obtained in the present experiments are analysed as involving the $^3\Pi$ (1) state for lower state. The constants for the lower state are such that they represent well the $\triangle G\,(v+\frac{1}{2})$ values obtained in the present experiments from $v = 0$ to $v = 26$ as well as those obtained by Brown from $v = 9$ to $v = 43$. The vibrational constants of the two states involved are:

ω_e''	$\omega_e''x_e''$	$\omega_e''y_e''$	$\omega_e z_e''$
137·8 cm.$^{-1}$,	0·571 cm.$^{-1}$,	−0·1156 cm.$^{-1}$	$3\cdot09\times10^{-3}$ cm.$^{-1}$

$\omega_e''t_e''$	ω_e'	$\omega_e'x_e'$
$-2\cdot5\times10^{-5}$ cm.$^{-1}$,	90·1 cm.$^{-1}$,	0·15 cm.$^{-1}$

The probable electronic configurations and electronic terms for the different observed states of IBr are discussed.

INTRODUCTION

IT was mentioned in the earlier paper[1] that IBr when excited in the presence of argon gives four band systems in the regions: (1) 5425–5360 Å, (2) 4520–4415 Å, (3) 4120–4010 Å and (4) 3915–3540 Å. Of these the first three were analysed and discussed in that paper and the last one will be analysed and discussed in this paper.

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EXPERIMENTAL RESULTS AND VIBRATIONAL ANALYSIS

The band system in the region 3915–3540 Å has been photographed with a 3-prism Steinheil glass spectrograph, a Hilger E_1 Littrow quartz spectrograph and a 21-feet grating spectrograph in the first order. Figures 1 and 2 show the system 3915–3540 Å as obtained with these different spectrographs. The wavelengths and wavenumbers of the band heads measured from the plates taken on the 21-feet grating spectrograph are given in Table I in which

TABLE I

Wavelengths, wavenumbers and intensities of the bands in the 3915–3540 Å system

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
0	3915·7	25531	1	3884·8	25734*
1	3914·0	25542*	1	3884·1	25739
1	3913·0	25549	4	3883·3	25744
1	3910·6	25564	3	3882·3	25751*
2	3908·3	25579	3	3881·4	25757
1	3906·2	25593	3	3877·9	25780
0	3904·5	25604*	5	3877·3	25784
0	3903·7	25609	10	3876·5	25789
2	3902·7	25616	4	3872·7	25814
3	3901·9	25621	5	3871·5	25822
2	3901·1	25627	5	3869·6	25835
1	3899·4	25638	5	3868·1	25844
1	3898·1	25646	10	3865·2	25864
2	3895·4	25664	3	3864·3	25871
5	3893·6	25676	3	3863·4	25877
4	3892·6	25683	2	3861·5	25889
2	3890·5	25696	10	3860·4	25897
1	3890·0	25700	3	3859·8	25901
4	3888·7	25708	5	3858·8	25907
2	3887·6	25716	2	3857·9	25914
2	3885·5	25729	2	3857·3	25918

TABLE I (*Contd.*)

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
0	3855·1	25932	1	3823·4	26147
9	3854·4	25937	5	3822·9	26151
4	3853·7	25941	5	3822·5	26153
4	3852·6	25949	1	3820·5	26167
5	3850·7	25962	2	3819·5	26174
3	3849·9	25967	3	3818·2	26183
3	3849·4	25971	2	3816·3	26196
3	3848·9	25974	2	3815·0	26205
3	3847·8	25982	2	3813·5	26215
4	3845·5	25997	3	3812·1	26225
0	3843·9	26008	3	3808·8	26248
2	3842·7	26016	2	3807·5	26257
8	3840·9	26028	2	3806·4	26264
8	3839·9	26035	3	3805·4	26271
2	3839·2	26040	0	3804·2	26279*
1	3838·5	26044	1	3803·5	26284*
3	3837·7	26050	4	3802·7	26290
3	3837·3	26053	4	3800·7	26304
3	3836·9	26055	4	3797·3	26327
7	3834·5	26072	2	3796·4	26333
2	3833·5	26079	2	3795·2	26342
3	3833·0	26082	3	3792·3	26362
3	3831·6	26091	3	3791·9	26364
1	3830·4	26100	3	3789·8	26379
4	3829·4	26107	3	3789·3	26382
3	3826·9	26123	2	3786·7	26401
3	3826·0	26130	2	3786·3	26404
5	3824·6	26139	3	3784·4	26417
5	3824·2	26142	3	3784·0	26420

TABLE I (*Contd.*)

I	λ_{air}	λ_{vac}	I	λ_{air}	λ_{vac}
2	3782·5	26430	2	3752·8	26639
1	3781·3	26438	3	3751·9	26646
3	3779·9	26448	3	3751·6	26648
3	3779·5	26451	1	3751·2	26651
3	3778·8	26456*	1	3749·9	26660
3	3778·4	26459	1	3749·0	26666
2	3777·2	26467	1	3748·1	26673
2	3776·3	26473	2	3747·2	26679
2	3775·5	26479	3	3746·6	26683
1	3775·1	26482	4	3745·5	26691
1	3773·9	26490	2	3742·5	26713
3	3772·4	26501	1	3741·5	26720
3	3772·1	26503	0	3739·4	26735
2	3770·2	26516	0	3738·3	26743
2	3769·4	26529	1	3737·4	26749*
?	3768·0	26532	0	3735·9	26760
1	3767·1	26538	1	3733·2	26779*
1	3765·3	26551*	1	3732·7	26783
2	3764·9	26554	1	3732·0	26788
4	3763·3	26565	1	3731·3	26793
4	3761·8	26575	1	3730·7	26797*
2	3760·2	26588	1	3728·1	26818
2	3758·3	26600	1	3727·3	26821
1	3757·6	26605	0	3726·5	26827
2	3757·2	26608	1	3723·6	26848
2	3756·7	26612*	2	3722·2	26858
2	3755·3	26621	2	3721·5	26864*
1	3754·9	26624*	1	3720·6	26870
0	3754·3	26629*	0	3720·2	26873

TABLE I (*Contd.*)

I	λ_{air}	λ_{vac}	I	λ_{air}	λ_{vac}
1	3719·6	26877	2	3683·6	27140
0	3718·7	26883	0	3682·4	27148
2	3717·2	26894	2	3680·1	27166
2	3716·8	26897	2	3678·9	27174
1	3714·9	26911	0	3676·5	27192
1	3713·8	26919	1	3675·4	27200*
1	3711·7	26934	0	3672·9	27219
0	3711·1	26939	0	3672·0	27225
2	3709·8	26948*	0	3671·5	27229
2	3709·0	26954	?	3670·6	27236
1	3708·1	26960	?	3670·0	27240
0	3707·2	26967	1	3669·2	27246
2	3704·5	26987	2	3668·2	27254
1	3702·3	27003	2	3667·9	27256*
1	3701·7	27007	2	3666·9	27263
1	3699·9	27020	1	3665·9	27271
1	3698·5	27030*	2	3664·3	27283*
1	3697·8	27035	2	3663·3	27290*
0	3696·3	27046	2	3662·3	27298
1	3695·3	27054	1	3661·5	27304
1	3694·4	27060*	0	3660·7	27310
2	3692·7	27073	1	3659·6	27318
2	3690·2	27091	2	3658·7	27324
1	3689·3	27098	2	3657·9	27331
0	3688·4	27104	1	3656·8	27338
1	3686·4	27119*	1	3655·8	27346
1	3686·0	27122*	0	3655·3	27350
1	3685·5	27125*	2	3654·6	27355
1	3684·6	27133	2	3653·5	27363

TABLE I (*Contd.*)

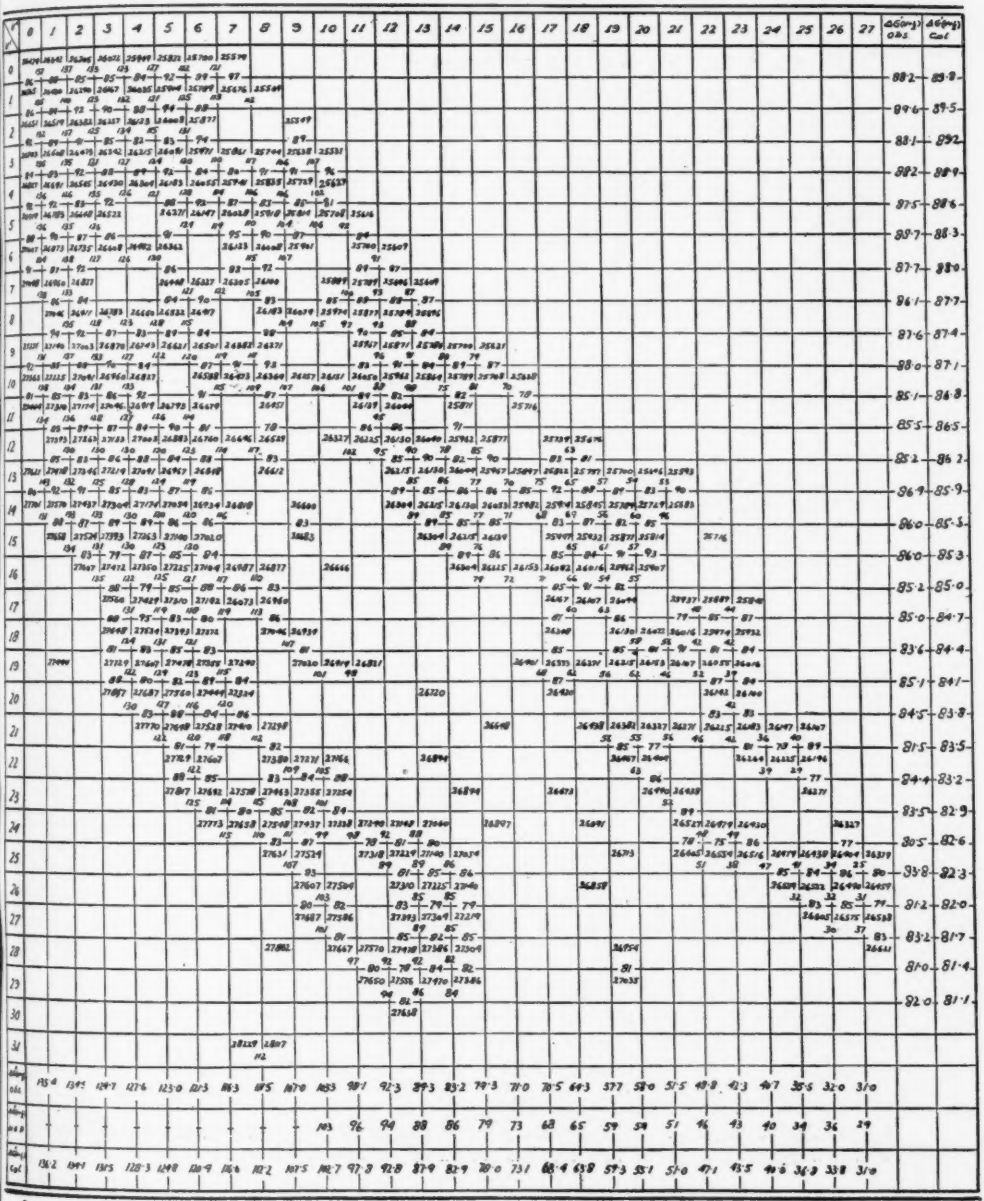
I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
2	3652·1	27374	1	3622·4	27598*
2	3651·2	27380	0	3621·3	27607
?	3650·5	27386	1	3620·3	27614*
0	3649·5	27393	?	3619·5	27621
2	3645·3	27410	1	3618·1	26631
2	3646·8	27413	1	3617·6	27635*
1	3644·8	27429	0	3617·2	27638
1	3643·8	27437	0	3616·9	27640*
0	3642·8	27444	1	3615·9	27648
0	3640·2	27463	2	3615·6	27650
1	3639·3	27470	2	3614·5	27658
1	3639·0	27472	1	3613·4	27667
0	3638·2	27478	1	3613·0	27670*
1	3634·7	27504	1	3612·5	27674*
1	3634·2	27509*	1	3610·8	27687
2	3632·1	27524	0	3610·2	27691
2	3631·6	27528	1	3609·0	27701
1	3629·0	27548	1	3605·3	27729
?	3627·9	27556	1	3600·0	27770
1	3627·5	27560	1	3599·6	27773
1	3626·1	27570	1	3593·9	27817
1	3625·6	27574	2	3585·6	27882
1	3625·1	27578*	1	3570·6	27999
2	3624·0	27586	1	3555·6	28117
0	3623·7	27589*	1	3541·5	28229

Note.—Bands marked (*) in the above table are not put in the vibrational scheme shown in Table II. Some of these bands can be accounted as isotopic bands and some can be put in Table II with error more than what is allowed for the bands put in that table.

the visually estimated relative intensities are also included. The error involved may be estimated to be about ± 2 cm.$^{-1}$ This band system is the most exten-

TABLE II

Vibrational scheme of the system 3915–3540 Å of IBr



sive of all the different band systems of IBr obtained in the present experiments. Haranath and Rao,[2] exciting IBr with a condensed transformer discharge, reported recently about 40 bands in the region 3900–3800 Å. They analysed the bands obtained by them as due to transition from an upper level at 38306 cm.$^{-1}$ with $\omega_e = 104$ cm.$^{-1}$ and $\omega_e x_e = 0{\cdot}8$ cm. to the $^3\Pi$ (1) state at $T_e = 12230$ cm.$^{-1}$ reported earlier by Brown[3] from the near infrared absorption band system. It was not possible to represent all the bands obtained in the present experiments with the above constants obtained by Haranath and Rao.* In fact even the 40 bands obtained by them are not well represented with these constants, as all the $\triangle G(v + \frac{1}{2})$ values observed according to their analysis are all higher than those calculated according to the constants they used. However, their view that the lower state involved for the system is the $^3\Pi$ (1) state is supported by the vibrational analysis given in this paper.

The Deslandres scheme of the band system representing all the bands is given in Table II and the corresponding intensity distribution in Table III.

The $\triangle G(v + \frac{1}{2})$ values obtained from Table II are listed in Table IV along with the $\triangle G(v + \frac{1}{2})$ values obtained by Brown[3] for the upper state $^3\Pi$ (1) of the near infrared absorption system of IBr. The two sets of the $\triangle G(v + \frac{1}{2})$ values are plotted against v in Fig. 3 and all the points could be represented well by a smooth curve. This suggests that both the sets of $\triangle G(v + \frac{1}{2})$ values represent the same electronic state. It was found that all the $\triangle G(v + \frac{1}{2})$ values can satisfactorily be represented with the constants $\omega_0 = 137{\cdot}05$ cm.$^{-1}$, $\omega_0 x_0 = 0{\cdot}74$ cm.$^{-1}$, $\omega_0 y_0 = 0{\cdot}1095$ cm.$^{-1}$, $\omega_0 z_0 = 3{\cdot}03 \times 10^{-3}$ cm.$^{-1}$ and $\omega_0' = 2{\cdot}5 \times 10^{-5}$ cm.$^{-1}$ The calculated $\triangle G(v + \frac{1}{2})$ values are also included in Table IV and plotted in Fig. 3. All the bands in Table I were thus found to be fairly well represented with the formula†

* Further because of the higher anharmonicity factor the dissociation energy of the upper state by linear extrapolation comes to only 3328 cm.$^{-1}$, giving 41431 cm.$^{-1}$ for the energy of dissociation products, whereas the nearest expected level of dissociation products are too far off from this. This would mean that the actual dissociation energy will be so many times higher than the D_0 obtained. Therefore it is necessary either to decrease the anharmonicity considerably if possible or to add up positive higher order terms so that the dissociation energy could be increased considerably. It may be also noted that the ν_e value of 26076 cm.$^{-1}$ given by them for this system is wrongly calculated, as it should be 25954·5 cm.$^{-1}$ according to their analysis.

† The linear extrapolation using the ω_0' and $\omega_0' x_0'$ of this formula gives $D_0' = 12500$ cm.$^{-1}$ which leads to the value of 52124 cm.$^{-1}$ for the energy of the dissociation products compared to the value of 41431 cm.$^{-1}$ that one gets from the constants used by Haranath and Rao.[2] This value of 52124 cm.$^{-1}$ is still lower than the nearest expected level of dissociation products. The actual D_0' is therefore larger than that one obtains by linear extrapolation and this is an indication that the state involved is probably an ionic state.[6,7] It is likely that certain positive higher order terms like $\omega_0' y_0' v'^3$ are involved which become appreciable at larger v' values than those observed and lead to a higher value for D_0' than that one obtains by linear extrapolation.

$$\nu = 26476 + (90{\cdot}0\,v' - 0{\cdot}15\,v'^2) - (137{\cdot}5\,v'' - 0{\cdot}74\,v''^2 - 0{\cdot}1095\,v''^3 + 3{\cdot}03\times10^{-3}\,v''^4 - 2{\cdot}5\times10^{-5}\,v''^5)$$

TABLE III

Intensity distribution and Frank-Condon parabola of the band system 3915–3540 Å

v'/v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
0	2	2	2	7	4	5	1	2																				
1	4	2	4	1	8	2	10	5	1																			
2	3	2	3	2	3		3																					
3	0	2	2	2	2	3	3	10	4	1	0																	
4			4	2	4	3	3	4	5	2	2																	
5	1	1	3	2		3	1	8	2	4	4	2																
6	1	0	0	2	1	3		3	0	3		1	0															
7	1	1	0			3	4	2	1		2	10	2	0														
8		0	1	1	1	1	3		3	2	3	3	5	2														
9	1	2	1	1	0	2	3	3	3			3	3	3	1	3												
10	1	0	2	1	0		2	2	3	2	5	3	5	10	10	4	1											
11	0	0	2	0	1	1	2		3			5	1		3													
12		0	2	1	1	0	0	3	0		4	3	3	2	5			1	5									
13	1	0	0	0	2	0	1		2	0			2	3	1	3	10	5	3	1	1	1						
14	1	1	1	1	2	1	1	1		2			4	2	3	3	3	2	5	10	2	4						
15		2	2	0	2	2	1		3				4	2	5		4	0	3	4		2						
16			0	1	0	0	0	2	1		1			4	3	5	3	2	5	5								
17				1	1	0	0	2	1								1	1	1		9	2	5					
18				1	2	0	1		0	0							3		3	7		3	0					
19		1		1	0	0	2	1		1	1	1				2	2	3	2	5	4	3	2					
20				1	1	1	0	2						1			3					3	1					
21					1	1	2	2	2							3			1	3	4	3	3	3	1	4		
22						1	0		2	1	2			2						2	2			2	3	2		
23						1	0	1	1	2	2				2			1			1	1				3		
24							1	2	1	1	1	1	0	1		2		4			3	2	2			4		
25									1	2		2	1	2	1					2		1	2	2	2	1	2	3
26										0	1		0	0	2				2						2	2	1	3
27										1	2		0	1	0											1	4	1
29									2		1	1	0	1	1					2								2
29												2	1	1	1					1								
30													0															
31								1	1																			

TABLE IV

The $\triangle G(v+\frac{1}{2})$ values for the $^3\Pi(1)$ state of IBr at $T_0 = 12148$ cm.$^{-1}$

v	Observed $\triangle G(v+\frac{1}{2})$ cm.$^{-1}$	Brown $\triangle G(v+\frac{1}{2})$ cm.$^{-1}$	Calculated $\triangle G(v+\frac{1}{2})$ cm.$^{-1}$
0	135·4	..	136·2
1	134·5	..	134·1
2	129·7	..	131·5
3	127·6	..	128·3
4	123·0	..	124·8
5	121·3	..	120·9
6	116·3	..	116·6
7	111·5	..	112·2
8	107·0	..	107·5
9	103·3	103	102·7
10	98·1	96	97·8
11	92·3	94	92·8
12	89·3	88	87·9
13	83·2	86	82·9
14	79·3	79	78·0
15	71·0	73	73·1
16	70·5	68	68·4
17	64·3	65	63·8
18	57·7	59	59·3
19	58·0	54	55·1
20	51·5	51	51·0
21	48·8	46	47·1
22	42·3	43	43·5
23	40·7	40	40·0
24	35·5	34	36·8
25	32·0	36	33·8
26	31·0	29	31·0
27	..	30	28·5
28	..	25	26·1
29	..	23	24·0
30	..	22	22·0
31	..	21	20·2
32	..	19	18·5
33	..	19	17·0
34	..	16	15·5
35	..	14	14·2
36	..	12	12·8
37	..	10	11·5
38	..	9	10·1
39	..	9	8·6
40	..	8	7·0
41	..	5	5·2
42	..	4	3·2
43	..	4	1·0

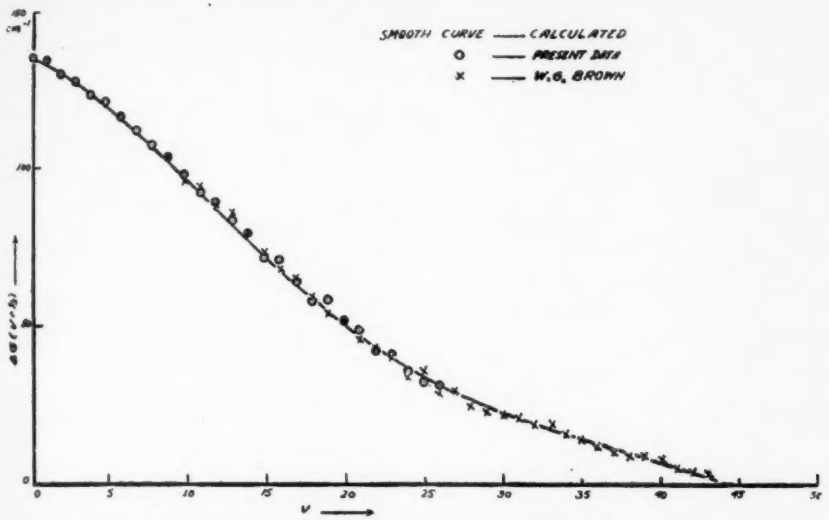


FIG. 3. The graph showing the $\triangle G(v+\frac{1}{2})$ *versus* v of $^3\Pi$ (1) state of I Brat $T_e = 12213$ cm.$^{-1}$

The deviation between the observed and calculated values of the band heads is mostly within $\pm$ 3 cm.$^{-1}$ and for some cases $\pm$ 4 cm.$^{-1}$ Only in very few cases it is $\pm$ 5 cm.$^{-1}$

As brown did not observe any bands with $v' > 9$ in the near infrared absorption band system, he had to use a long extrapolation to obtain ν_e and ω_e of the upper state of the absorption band system. The $\triangle G(v+\frac{1}{2})$ values for this level are known from the present experiments upto $v = 0$ and therefore it is not necessary to use such a long extrapolation. Using the vibrational constants obtained above for this state along with the absorption data of Brown, the T_0 and T_e for this level are obtained to be 12148 cm.$^{-1}$ and 12213 cm.$^{-1}$ respectively. The position of the upper level of the system thus comes out to be $T_0 = 38624$ cm.$^{-1}$ or $T_e = 38714$ cm.$^{-1}$

Isotopic Shift

As bromine has two equally abundant stable isotopes Br^{79} and Br^{81}, each vibrational band of the IBr system is expected to be doublet. But the bands in the system 3915–3540 Å lie very much close together and overlap one another, so that it is difficult to identify any isotopic shift unambiguously.

Electronic Transitions Involved

The positions of all the stable states of IBr molecule including those observed by the earlier workers are given along with the vibrational constants in Table V. The band systems to which the different levels are responsible

TABLE V

*Observed States of Iodine Bromide Molecule**

Electronic Configuration in terms of molecular orbitals No. of[f]				Electron States		Name[d,g]	Position of the levels[e] cm.$^{-1}$		ω_0 cm.$^{-1}$	ω_e cm.$^{-1}$	Dissociation products[e]	Remarks
σ	π	π	σ^*	Case a or b type	Case c or Ω-s type		T_0	T_e				
..	..	..	..	..	..	I	$a_0+24524$	$a_e+24540$	128·3	128·4	*ex*	I⟶H gives emission bands in the region 4120–4010 Å in the presence of argon (Ref. 1)
..	..	..	..	..	..	H	a_0	a_e	159·5	160·6	*ex*	..
2	4	3	$\sigma^\times$	..	$\Pi_{1,0+}$	G	56369	..	(310)	..	*ex*	X⟶G gives absorption bands in the vacuum ultraviolet region (Cordes and Sponer[5])
2	4	3	$\sigma^\times$	..	Π_1	F	51701	..	(314)	..	*ex*	X⟶F gives absorption bands in the vacuum ultraviolet region (Ref. 5)
2	3	3	2	$^1\Sigma^+$	0^+	E	39030	39126	76·5	77·0	*ex*	E⟶B′ gives emission band system in the region 4520–4415 Å in the presence of argon (Ref. 1)
2	3	3	2	$^1\Delta$	2	D	38623	38713	90·0	90·1	*ex*	D⟶A gives emission band system in the region 3915–3540 Å in the presence of argon (discussed in the present paper)
2	3	3	2	$^3\Sigma^-$	1 or 0^+	C	35314	35427	43·0	43·03	*ex*	C⟶B′ gives emission band system in the region 5425–5360 Å in the presence of argon (Ref. 1)
2	3	4	1	$^3\Pi$	0^+	B′	16712	16814	65·3	65·5	*bb*	X⟶B′ gives absorption bands in the region 6186–5458 Å (Brown[3])
2	4	3	1	$^3\Pi$	0^+	B	16112	16155	(145·7)	(150)	*ab*	X⟶B gives absorption bands in the region 6764–6240 Å (Brown[3])
2	4	3	1	$^3\Pi$	1	A	12148	12213	137·1	137·8	*aa*	X⟶A gives absorption bands in the region 8000–6817 Å (Brown[3])
2	4	4	0	$^1\Sigma^+$	0^+	X	0	0	267·6	268·4	*aa*	Ground State

* The term scheme is mainly based upon that given by Mulliken[4] for ICl.

[e] Under dissociation products *aa* mean I $^2P_{3/2}$ + Br $^2P_{3/2}$ atoms, *ab* means I $^2P_{3/2}$ + Br $^2P_{\frac{1}{2}}$ atoms, *bb* means I $^2P_{\frac{1}{2}}$ + Br $^2P_{\frac{1}{2}}$ atoms and *ex* means either iodine and bromine ions or iodine and bromine atoms of which one, at least, is excited.

[d] The names to the levels are given according to their heights. The designations for the levels at 56369 and 51701 cm.$^{-1}$ are now G and F instead of D and C used by Herzberg.

[e] The values given in brackets ( ) are only approximate.

[f] In this column σ represents a bonding orbital of the form $(4p\sigma_{Br} + 5p\sigma_I, \sigma)$. π, π represent orbitals of the form $(4p\pi_{Br} + 5p\pi_I)$, $(5p\pi_I - 4p\pi_{Br})$ if molecular orbital approximation is used) for the π electrons. If atomic orbital approximation is used for the π electrons, π, π in the first column of the table stands for $4p\pi_{Br}$ and $5p\pi_I$ respectively. $\sigma^\times$ stands for $(5p\sigma_I - 4f\sigma_{Br})$ which is anti-bonding. σ^* stands for an orbital of the electron which has gone to $(n+1)s\sigma$ orbit from $np\pi$ orbit.

[g] The levels named C, D and E may be having positive higher order vibrational constants (like $\omega_e y_e v^3$, etc.) which becomes significant at higher vibrational levels than those observed and take the dissociation limits to higher proper positions than those one would get by linear extrapolation.

are given in the last column of the table. It is more difficult in the case of IBr than in the case of I_2 and Br_2 to determine the electronic configurations and the electronic terms for the different observed levels. This is because the absence of the *gerade* and *ungerade* classification of the terms increases the number of the allowed transitions. However, with the help of term scheme developed by Mulliken[4] for ICl and taking analogies from I_2 and Br_2 molecules, it is possible to arrive at certain tentative conclusions about the electronic configurations and electronic terms of the states involved.

The electronic configurations and the electronic terms, responsible for the states X, A, B, B′, F and G given in Table V, are those suggested by Mulliken.[4] The new states that are observed in the present experiments are C, D, and E at 35314 cm.$^{-1}$, 38623 cm.$^{-1}$ and 39030 cm.$^{-1}$ respectively and H and I at undetermined positions 'a_0' and 'a_0' + 25244 cm.$^{-1}$ respectively. Of these the states C and E form the upper levels of the systems 5425–5360 Å and 4520–4415 Å respectively discussed in the earlier paper.[1] The state D forms the upper level of the 3915–3540 Å system discussed in this paper. All these states have very low vibrational frequencies and it is quite likely that the electronic configurations for these states will involve two anti-bonding σ electrons. The first two such electronic configurations according to Mulliken[4] are $\sigma^2\pi^4\pi^3\sigma^*$ and $\sigma^2\pi^3\pi^3\sigma^{*2}$. Of these the $\sigma^2\pi^4\pi^3\sigma^*$ configuration gives the states $^1\Sigma^+$ (0$^+$), $^1\Delta$ (2) and $^3\Sigma^-$ (1, 0$^+$) which according to Mulliken's Table‡ for ICl as well as on analogy with similar states of I_2 and Br_2, are expected to dissociate into normal $^2P + {}^2P$ atoms of iodine and bromine. It is, therefore, likely that the configuration $\sigma^2\pi^3\pi^3\sigma^{*2}$ is responsible for the three states C, D and E. The configuration $\sigma^2\pi^3\pi^3\sigma^{*2}$ gives rise to the electronic terms $^1\Sigma^-$ (0$^-$), $^3\Delta$ (3, 2, 1), $^3\Sigma^+$ (1, 0$^-$), $^1\Sigma^+$ (0$^+$), $^1\Delta$ (2) and $^3\Sigma^-$ (0$^+$, 1) of which the first three are expected to dissociate into normal $^2P + {}^2P$ iodine and bromine atoms and are, therefore, probably repulsive states whereas the last three are expected to dissociate into iodine and bromine ions or into iodine and bromine atoms of which one, at least, is in excited state and therefore, they are probably stable. The three electronic terms $^1\Sigma^+$ (0$^+$), $^1\Delta$ (2) and $^3\Sigma^-$ (0$^+$ or 1) can, therefore, be tentatively assigned to the states E, D and C respectively. It may be noted that the ω_e values for the different states arising from the same configuration are expected to be nearer to one another, but the ω_e value for the C state is only 43·03 cm.$^{-1}$ whereas the ω_e values for

‡ Incidentally it may be mentioned that Haranath and Rao[2] appear to have overlooked the details given by Mulliken's Table[4] and state wrongly that the states arising in the configuration $\sigma^2\pi^4\pi^3\sigma^*$ are predicted by Mulliken to dissociate into $I^+ + Cl^-$.

for an orbital of the electron which has gone to $(n+1)s\sigma$ orbit from $np\pi$ orbit.
* The levels named C, D and E may be having positive higher order vibrational constants (like $\omega_e y_e^{(2)}$, etc.) which becomes significant at higher vibrational levels than those observed and take the dissociation limits to higher proper positions than those one would get by linear extrapolation.

the D and E are 90·1 and 77·0 cm.$^{-1}$ respectively. This may be because these states might be having different dissociation products.§

The assignment of electronic configurations for the H and I states will be more difficult than the assignment for the levels C, D and E, as even the exact positions of these levels are not yet determined. The electronic configurations for the states H and I are, therefore, not included in Table V.

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§ The $^3\Pi_u(I_u)$ and $^3\Pi_u(O_u^+)$ states of iodine arising from the same configuration $\sigma_g^2\pi_u^4\pi_g^3\sigma_u$ are known to have ω_e values 40 and 128 cm.$^{-1}$ respectively which is understood on the basis that they have different dissociation products.

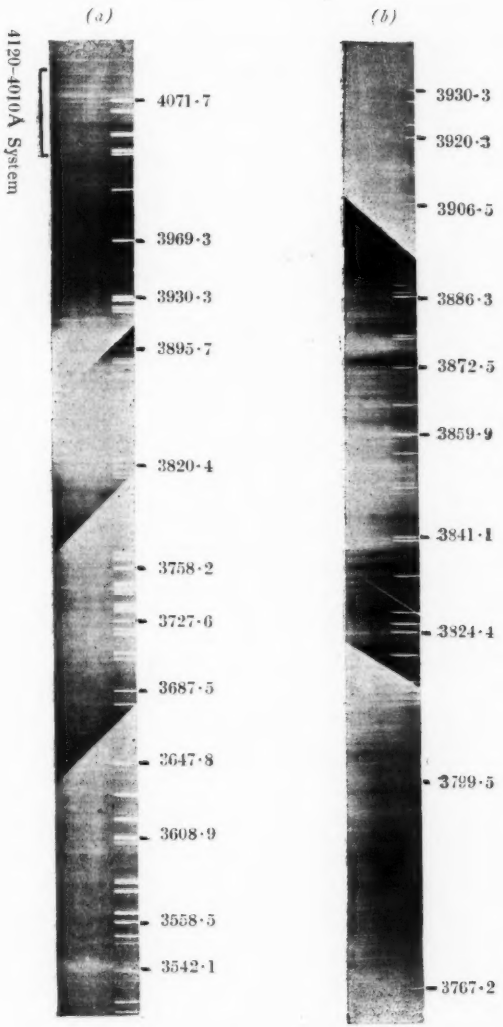

FIG. 1.

(*a*) Enlargement of the spectrum of IBr excited in the presence of argon taken with a Hilger E_1 Littrow quartz spectrograph in the region 4120–3540 Å. (*b*) Enlargement of the band system 3915–3540 Å of IBr taken with Steinheil 3-prism glass spectrograph in the region 3930–3760 Å.

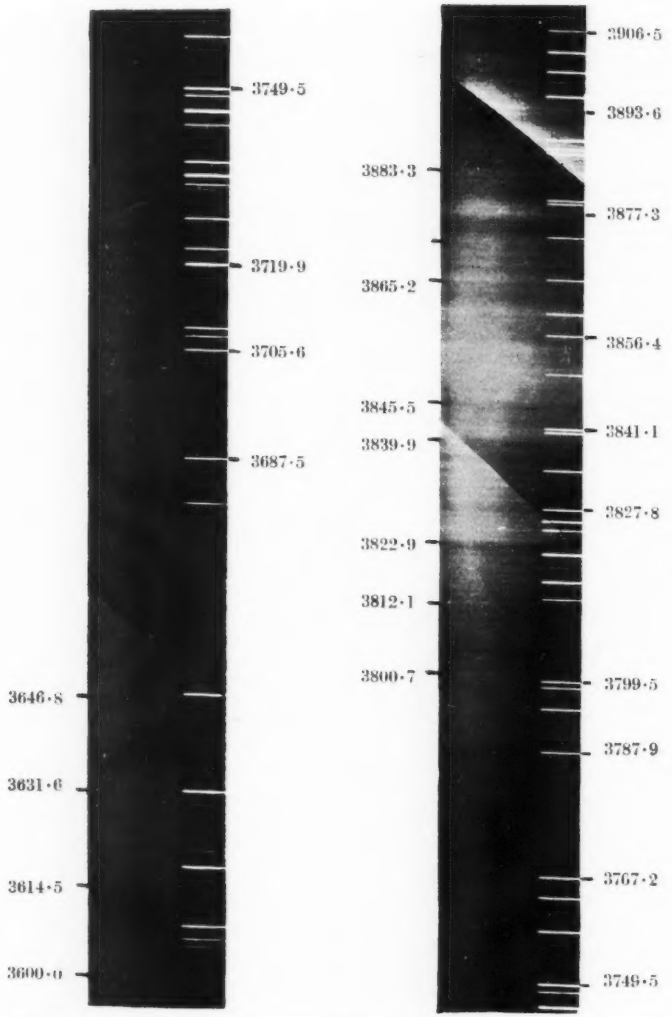

FIG. 2. Enlargement of 3915–3540 Å system of IBr taken with 21-feet grating spectrograph in the first order.

HETEROCYCLIC COMPOUNDS

Part XII.* Synthesis of 2-Keto-4-Phenyl-2, 3, 4, 6-Tetrahydro-1-Thieno (3, 4)-Imidazole

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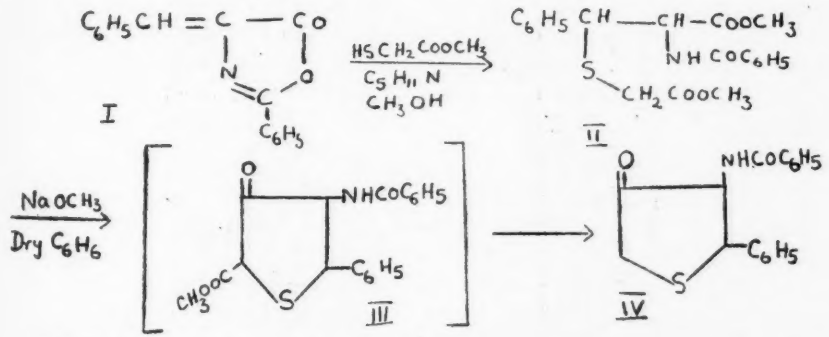
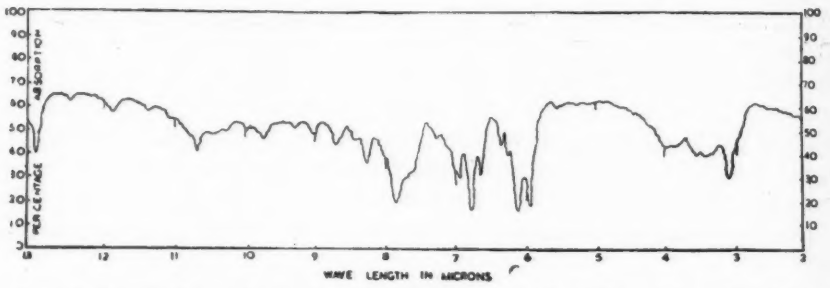
Synthesis of analogues of biotin is an attractive endeavour and certain investigations were initiated to achieve the same. Circumstances have made it difficult for the author to pursue the scheme of work originally contemplated and so the result of work so far completed is reported. Brown, Safir, Baker, Bernstein and Dorfman obtained 2-keto-4-methyl-2, 3, 4, 6-tetrahydro-1-thieno-(3, 4)-imidazole by a series of reactions, starting from the azlactone of α-benzamido crotonic acid. This reacted with thioglycollic ester to yield, α-benzamido-β-carbethoxy methyl thiobutyrate. Dieckmann cyclisation followed by hydrolysis and treatment with potassium cyanate gave the desired imidazole. It was thought profitable to synthesise the substance mentioned in the title of this paper by an analogous series of reactions:

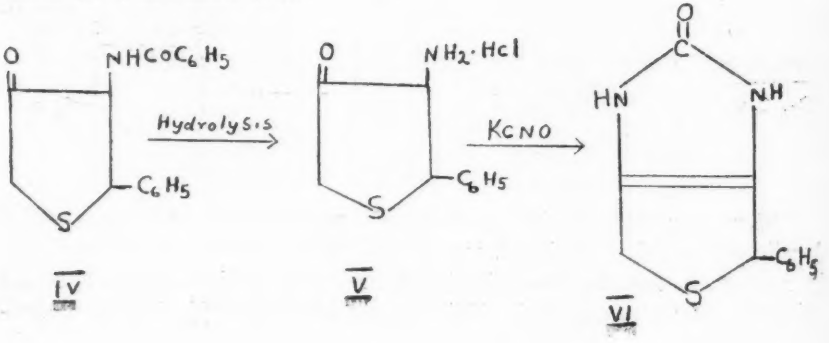


When a mixture of the azlactone of benzaldehyde and methyl thioglycollate in absolute methanol was treated with a few drops of piperidine, the mercaptan added to the double bond, the azlactone ring opened and the carboxyl group was esterified. This gave in one step 82% yield of methyl-

α-benzamido-β-carbmethoxy phenyl thio-butyrate (II) as a viscous oil. It solidified on titurating with petrol and was crystallised from light petrol (40°–60°) yielding colourless crystals melting at 95–97°. The thioether (II) underwent Dieckmann reaction in the presence of sodium methoxide to give 2-phenyl-3-benzamido-4-keto-thiophane (IV) in 50% yield. The decarboxylation, probably elimination as carbonate, could not be prevented experimentally; which is a circumstantially favourable position when it is desired to introduce a side chain in position five by condensation with appropriate aldehydes. The cyclisation product was soluble in water but could be completely extracted by continuous ether extraction. It crystallised from ethanol, m.p. 236°. That elimination of the ester group had taken place during cyclisation was established by analysis and infra-red data. The ketone gave a 2, 4-dinitrophenyl hydrazone melting at 185°. The 2-phenyl-3-benzamido-4-keto-thiophane (IV) was hydrolysed by a mixture of hydrochloric and



phosphoric acids, when the hydrochloride of 2-phenyl-3-amino-4-keto-thiophane (V) was obtained. It crystallised from concentrated hydrochloric acid melting at 94°. The pure hydrochloride dissolved in water was treated with potassium cyanate to afford 2-keto-4-phenyl-2, 3, 4, 6-tetrahydro-1-thieno-(3, 4)-imidazole (VI).



Experimental

Methyl-α-benzamido-β-carbmethoxy phenyl thio-butyrate (II)

To the azlactone (12·5 g.) in absolute methanol (100 ml.) was added methyl thioglycollate (5·3 g.) and a few drops of piperidine. The azlactone went into solution slowly and after the mixture was allowed to stand at room temperature for 3 days, was refluxed on the steam-bath for an hour. The excess of methanol was removed under reduced pressure and the residual oil was poured on to ice under vigorous stirring. The pasty mass that separated was taken up in ether, the solution dried over anhydrous magnesium sulphate and the ether removed. The product was repeatedly crystallised from light petrol (40°–60°) and after hard crystals were obtained, purified by further crystallisation from dilute acetic acid. Yield 15 grams (82%), m.p. 95°.

Found:	C, 61·9	H, 5·3	N. 3·4
Calculated for $C_{20}H_{21}SO_5N$ ..	C, 62·0	H, 5·4	N, 3·6

2-Phenyl-3-benzamido-4-keto thiophane (IV)

The thiobutyrate (4 g.) in dry benzene (100 ml.) was added to sodium methoxide prepared from 0·6 gram of sodium and the mixture allowed to stand overnight. It was then refluxed for 18 hours and then poured on to ice with vigorous stirring. The benzene layer was removed and the aqueous portion extracted with benzene. The aqueous solution was cooled in ice and acidified with acetic acid and then continuously extracted with ether. The ethereal solution was dried over anhydrous magnesium sulphate and the ether removed. The resulting product was crystallised from ethanol yielding 1·5 grams (50% yield) of the pure product of m.p. 236°.

Found:	C, 68·6	H, 5·0	N, 4·9	S, 10·1
Calculated for $C_{17}H_{15}SNO_2$ ..	C, 68·7	H, 5·1	N, 4·8	S, 10·8

Infra-red spectrum data.—The data confirms the structure assigned to the product (please see curve). The compound absorbed in the region 770 cm.$^{-1}$ characteristic of $-CH_2-S-CH_2-$grouping. The absorptions in the regions 1683 cm.$^{-1}$, 1633 cm.$^{-1}$, 1683 cm.$^{-1}$, and 3224 cm.$^{-1}$ are characteristic of the keto group, the NH—CO—R and the —NH groups. That the compound exists in the enolic form is indicated by its absorption in region 3224 cm.$^{-1}$

2-Phenyl-3-amino-4-keto thiophane hydrochloride

2-Phenyl-3-benzamido-4-keto-thiophane (0·5 g.) was added to a mixture of orthophosphoric acid (1·0 ml.) and water (2·0 ml.) and the mixture

refluxed for an hour. Hydrochloric acid (10 ml.) was then added in two lots and refluxing continued for 5 hours. On cooling the hydrochloride separated out. It was collected and crystallised from concentrated hydrochloric acid. Yield 0·4 gm., m.p. 94°. This product was not analysed but was used immediately for the next step.

2-*Keto*-4-*phenyl*-2, 3, 4, 6-*tetrahydro*-1-*thieno*-(3, 4)-*imidazole* (*VI*)

The hydrochloride (200 mg.) was dissolved in water (3 ml.) and potassium cyanate (200 mg.) added. A clear solution was obtained, which was allowed to stand at room temperature for a day and then evaporated to dryness over a low boiling water-bath. The residue was repeatedly extracted with ethyl acetate, the solvent removed and the residue crystallised from acetone. Yield 50 mg., m.p. 130°.

Found:	.. C, 60·4	H, 4·5	N, 12·9
Calculated for $C_{11}H_{10}N_2SO$	.. C, 60·5	H, 4·6	N, 12·8

ACKNOWLEDGEMENT

I take this opportunity to thank Dr. K. N. Menon for suggesting this problem and for guidance and help during its execution. I thank the Government of India for a scholarship, Dr. Gurubakh Singh of the National Physical Laboratory for the Infra-Red Spectrum and Mr. S. Selvavinayakam for analysis.

SUMMARY

The synthesis of 2-Keto-4-phenyl-2, 3, 4, 6-tetrahydro-1-thieno-(3, 4)-imidazole is reported.

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TRANSFORMATIONS IN THE FUNCTIONAL SPACE OF QUANTUM MECHANICS

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Summary

It is shown that, apart from arbitrary point transformations, only linear transformations are allowed in the functional space. In particular, it is not possible to construct a Riemannian geometry in the functional space considered here.

1. Introduction

It is well known that we need today a generalization of quantum mechanics which can include the newly discovered particles in its scheme as well as get rid of the difficulties encountered in the field theories. In such a generalization, the interactions among the various particles would be described by some non-linear terms which should arise in the theory in a natural way. In a recent paper the author (1956) made an attempt in this direction by drawing an analogy between the relativity and the quantum theories. It was shown there that the components ψ^m of the state vector in quantum mechanics correspond to the components v^μ of the four-velocity of a particle in relativity. One can, therefore, introduce co-ordinates, χ^m, $\bar{\chi}^m$, corresponding to the co-ordinates x^μ of a particle, such that the time derivatives of χ^m and $\bar{\chi}^m$ equal ψ^m and $\bar{\psi}^m$:

$$\frac{d\chi^m}{dt} = \psi^m, \quad \frac{d\bar{\chi}^m}{dt} = \bar{\psi}^m.$$

Proceeding now in analogy with the development of the theory of general relativity from that of special relativity, we can introduce quite general non-singular transformations of χ and $\bar{\chi}$:

$$\chi^{m'} = \chi^{m'}(\chi^1, \chi^2, \ldots\ldots, \chi^N) \tag{1 a}$$

$$\bar{\chi}^{m'} = \bar{\chi}^{m'}(\bar{\chi}^1, \bar{\chi}^2, \ldots\ldots, \bar{\chi}^N), \quad m = 1, 2, \ldots\ldots, N. \tag{1 b}$$

The metric η, used in calculating the probability density, can now be considered as a function of χ and $\bar{\chi}$ and a tensor calculus for this space can be developed. It was found in the above paper that, though the wave equation obtained in this way was non-linear as expected, so long as one considered ψ and $\bar{\psi}$ to be the physical quantities of interest in the usual way, the expectation values of all dynamical variables would be the same in this theory as in the ordinary theory. There is, however, a possibility that χ and $\bar{\chi}$ may be physically significant and not ψ and $\bar{\psi}$. In that case, the formalism developed in the above paper would be of interest.

In the work mentioned above, the author considered a space of finite dimensions, N. It is of interest to inquire whether the formalism can be extended to functional space in which the χ's and the $\bar{\chi}$'s are labelled by a continuous variable, say x, instead of the discrete index m. This would be a generalization of the complex Riemannian space similar to that made by Dirac (1947) for the Hilbert space. It is the purpose of this note to examine this possibility.

2. Transformations in Functional Space

Let us see what the analogue of (1 a) for the continuous case would be. We label different representations by different letters and different points of the same representation by putting primes over that letter. Thus, in the x-representation, we write χ as $\chi(x)$; the function χ at different points x', x'', etc., will be denoted by $\chi(x')$, $\chi(x'')$, etc. In (1 a) the new $\chi^{m'}$ may depend on all the old χ's. Its analogue would now be

$$\chi(y) = \int \mathrm{F}_y\big(\chi(x)\big)\, dx, \tag{2}$$

where F_y is an arbitrary function of its argument.

Let us now make a transformation from the y- to the z-representation:

$$\chi(z) = \int \mathrm{F}_z\big(\chi(y)\big)\, dy \tag{3}$$

where F_z may be a different function of its argument than F_y. Using (2) in (3), we get

$$\chi(z) = \int \mathrm{F}_z\left(\int \mathrm{F}_y\big(\chi(x)\big)\, dx\right) dy. \tag{4}$$

In order that our transformations may have the group property, we should be able to write (4) as

$$\chi(z) = \int G\left(\chi(x)\right) dx, \tag{5}$$

where G is some function of $\chi(x)$. It is clear from an inspection of (4) that this can be done only if the integral over x occurs linearly in F_z; that is, we must have

$$F_z\left(\int F_y\left(\chi(x)\right) dx\right) = f(z, y) \int F_y\left(\chi(x)\right) dx, \tag{6}$$

where $f(z, y)$ is some function of z and y. Using (2) in (6), we get

$$F_z\left(\chi(y)\right) = f(z, y)\, \chi(y), \tag{7}$$

that (3) becomes

$$\chi(z) = \int f(z, y)\, \chi(y)\, dy. \tag{8}$$

This is of the same form as the linear transformations considered in the usual quantum mechanics. Thus, in the functional space that we are considering, only linear transformations are allowed.

3. More General Transformations

One may like to generalize the transformations (2) by letting F_y depend on two χ's referring to different points:

$$\chi(y) = \int\int F_y\left(\chi(x'), \chi(x'')\right) dx'dx''. \tag{9}$$

We shall now show that (9) again leads to linear transformations of the kind (8).

Let us again make a transformation from the y- to the z- representation:

$$\chi(z) = \int\int F_z\left(\chi(y'), \chi(y'')\right) dy'dy'' \tag{10}$$

and use (9) in (10):

$$\chi(z) = \int\int F_z\left(\int\int F_{y'}\left(\chi(x'), \chi(x'')\right) dx'dx'',\right.$$
$$\left.\int\int F_{y''}\left(\chi(x'), \chi(x'')\right) dx'dx''\right) dy'dy''. \tag{11}$$

The group property requires that we should be able to write (11) in the form

$$\chi(z) = \int\int G\left(\chi(x'), \chi(x'')\right) dx'dx''. \tag{12}$$

As before, this is possible only if F_z in (11) involves its arguments linearly:

$$F_z\left(\int\int F_{y'}\left(\chi(x'), \chi(x'')\right) dx'dx'', \int\int F_{y''}\left(\chi(x'), \chi(x'')\right) dx'dx''\right)$$
$$= f_1(z, y', y'') \int\int F_{y'}\left(\chi(x'), \chi(x'')\right) dx'dx''$$
$$+ f_2(z, y', y'') \int\int F_{y''}\left(\chi(x'), \chi(x'')\right) dx'dx'' \qquad (13)$$

or, using (9),

$$F_z\left(\chi(y'), \chi(y'')\right) = f_1(z, y', y'')\chi(y')$$
$$+ f_2(z, y', y'')\chi(y''). \qquad (14)$$

Here f_1 and f_2 are some functions of z, y' and y''. The equation (10) can now be written as

$$\chi(z) = \int\int [f_1(z, y', y'')\chi(y') + f_2(z, y', y'')\chi(y'')]\, dy'dy''$$
$$= \int\int [f_1(z, y', y'') + f_2(z, y', y'')]\chi(y')\, dy'dy''$$
$$= \int f(z, y')\chi(y')\, dy', \qquad (15)$$

where

$$f(z, y') = \int [f_1(z, y', y'') + f_2(z, y'', y')]\, dy''. \qquad (16)$$

The relation (15) is of the same form as (8), which proves the statement made at the beginning of this section.

4. Point Transformations

One can also consider transforamtions in which the new χ's (denoted here by $\chi'(x)$) are arbitrary functions of the old χ's:

$$\chi'(x) = \chi'\left(\chi(x)\right). \qquad (17)$$

While it may be of mathematical interest to look into these point transformations, they do not appear to be of importance in quantum mechanics. Therefore we do not examine them here.

One can also generalize (2) by having

$$\chi'(y) = G\left(\int F_y\left(\chi(x)\right) dx\right) \qquad (18)$$

where G is an arbitrary function. Such transformations can, obviously, be compounded from transformations of the kinds (2) and (17):

$\chi(x) \rightarrow \chi(y)$ in accordance with (2),

$\chi(y) \rightarrow \chi'(y)$ in accordance with (17).

5. Conclusion

We conclude that, apart from point transformations of the type (17), only linear transformations are allowed in the functional space. In particular, it is not possible to construct a Riemannian geometry in this space.

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MODIFICATIONS IN THE IODINE OXIDATION OF HYDROXY FLAVANONES AND THEIR METHYL ETHERS

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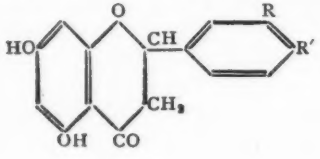
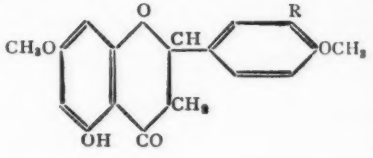
In a previous publication[1] the action of iodine and silver acetate on flavanones in absolute alcoholic solution was discussed. Naringenin (I *a*) and hesperetin (I *b*) were found to yield the corresponding 3-acetoxy-flavanones while naringenin dimethyl ether (II *a*) and 5:7-dimethoxy-flavanone (III *a*) yielded the corresponding 3-iodo-compounds (IV *a* and III *b*). Considerable difference was recorded regarding the behaviour of these 3-iodo-compounds towards alcoholic potash. The 3-iodo-5-hydroxy-7:4′-dimethoxy flavanone (IV *a*) on treatment with this reagent yielded the corresponding flavone, apigenin-7:4′-dimethyl ether (V *a*) while the 3-iodo-5:7-dimethoxy flavone was reported to yield the corresponding flavonol, galangin-5:7-dimethyl ether (VI *a*). A more detailed study of these reactions has now been made.



I

(*a*) R=H, R′=OH.

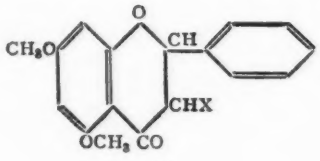
(*b*) R=OH, R′=OCH_3.



II

(*a*) R=H.

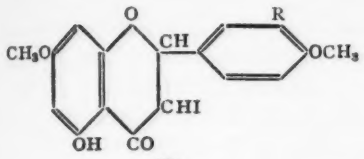
(*b*) R=OCH_3.



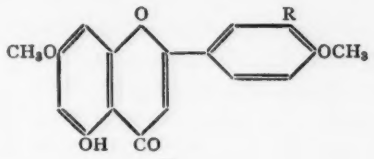
III

(*a*) X=H.

(*b*) X=I.



IV



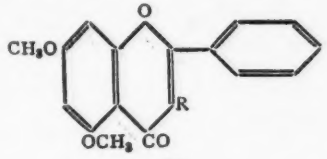
V

(*a*) R=H.

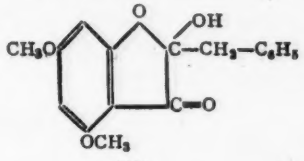
(*b*) R=OCH_3.

In the original procedure of Goel, Narasimhachari and Seshadri,[1] iodine was added to a boiling absolute alcoholic solution of the hydroxy flavanone and silver acetate. The method has not proved to be satisfactory as appreciable quantities of by-products are formed, making the purification of the main product difficult. During the course of the present work it has been found that if iodine is added at room temperature with shaking instead at the temperature of boiling alcohol and the addition is followed by refluxing for two hours, the purification of the product is simpler. Using this modified method naringenin (I *a*), naringenin-7: 4′-dimethyl ether (II *a*) and 5: 7-dimethoxy-flavanone (III *a*) have given good yields of 3-acetoxy-naringenin, 3-iodo-5-hydroxy-7: 4′-dimethoxy flavanone (IV *a*) and 3-iodo-5: 7-dimethoxy flavanone (III *b*) respectively. Similarly hesperetin (I *b*) gives a good yield of 3-acetoxy hesperetin and hesperetin 7: 3′-dimethyl ether forms the 3-iodo-compound (IV *b*).

Treatment with pyridine or with alcoholic potash of 3-iodo-naringenin-7: 4′-dimethyl ether (IV *a*) and of 3-iodo-hesperetin-dimethyl ether (IV *b*) yielded apigenin-7: 4′-dimethyl ether (V *a*) and luteolin-7: 3′: 4′-trimethyl ether (V *b*) respectively. 3-Iodo-5: 7-dimethoxy-flavanone (III *b*) behaved somewhat differently; when treated with pyridine it yielded chrysin dimethyl ether (VI *b*), whereas on treatment with alcoholic potash it gave a mixture of chrysin dimethyl ether (VI *b*), 3-hydroxy-5: 7-dimethoxy flavone (VI *a*) and 2-hydroxy-2-benzyl-4: 6-dimethoxy coumaranone (VII). The separation of this mixture has been effected by using the difference in the solubilities of the components in aqueous alkali of different concentrations.



VI



VII

(*a*) R=OH.

(*b*) R=H.

A probable explanation of the above difference in behaviour of the iodo-flavanones with alkali, may be found in the relative stability of the flavanone structures concerned. In the case of 3-iodo-5: 7-dimethoxy flavanone (III *b*) only a portion seems to react in the original flavanone form and undergo loss of hydrogen iodide to yield the corresponding flavone (VI *b*). But the greater portion seems to undergo other changes as the result of substitution of iodine by hydroxyl and ring opening. The major product is found to be 2-hydroxy-2-benzyl-4: 6-dimethoxy-coumaranone (VII) arising from ring closure in a different way. A small yield of the corresponding flavonol, galangin-5: 7-dimethyl ether (VI *a*), is also formed as the result of dehydrogenation of the 3-hydroxy flavanone of the appropriate configuration[2] (equatorial hydroxyl). On the other hand in the case of the dimethyl ethers of naringenin and hesperetin (II *a* and II *b*), on account of the presence of a free hydroxyl group in the 5-position, the flavanone structure has greater stability; when treated with alcoholic potash the oxide ring does not open out so readily and only removal of hydrogen iodide takes place producing apigenin-7: 4′-dimethyl ether (V *a*) and luteolin-7: 3′: 4′-trimethyl ether (V *b*).

A modification in the iodine oxidation of hydroxy flavanones to flavones using fused potassium acetate in glacial acetic acid and iodine has been recently reported.[3] By this modified method naringenin (I *a*) and hesperetin (I *b*) have been reported to undergo smooth conversion (60–70%) to yield the corresponding flavones, apigenin and diosmetin respectively. Since there is a special difference between the hydroxy flavanones and their partial methyl ethers in the action of iodine and silver acetate in absolute alcohol, a typical example, hesperetin dimethyl ether, has also been examined by this method.[3] The flavone, luteolin-7: 3′: 4′-trimethyl ether (V *b*), is obtained in less yield and it is accompanied by the corresponding 3-iodo-flavanone (IV *b*). The separation of this mixture is best effected by fractional precipitation from ethyl acetate solution using light petroleum. The iodo-flavanone could however be converted into flavone by the action of pyridine. It was identical with the sample obtained by the action of iodine and silver acetate. It would now appear that though it is the exclusive product when silver acetate is employed, it happens to be produced as a minor product even when potassium acetate is used.

EXPERIMENTAL

3-*Acetoxy-naringenin*

The modified procedure now employed is as follows: To a mixture of naringenin (1 g.) and silver acetate (2 g.) in absolute alcohol

(60 c.c.) was added iodine in the same solvent (0·85 g. in 40 c.c.) gradually during one hour with constant shaking at room temperature (20° C.). The iodine was decolourised within a few minutes of addition. The mixture was then either refluxed for 2 hours or allowed to stand at room temperature for 24 hours, the silver salt filtered off and the alcohol evaporated to dryness when a pale yellow coloured solid separated. It was first crystallised from ethyl acetate and light petroleum mixture and later from ethanol when it separated as tiny prisms (0·65 g.), m.p. 228–30° (decomp.).[1]

3-Hydroxy naringenin

The hydrolysis by means of acid has been carried out as follows; the earlier method using alkali[1] was not fully satisfactory.

The above compound (0·3 g.) was refluxed with alcoholic hydrochloric acid (1 : 1, 20 c.c.) for half an hour. The alcohol was removed under reduced pressure and the solution diluted with water to 200 c.c. A pale brown solid separated which was repeatedly extracted with ether (total vol. 200 c.c.). After evaporating the ether the residue was crystallised from aqueous alcohol yielding flesh coloured rhombohedral prisms (0·18 g.), m.p. 238–40° (*d*). It agreed in m.p. and colour reactions with an authentic sample of 3-hydroxy naringenin obtained by Fenton's oxidation[4] and the mixed m.p. was undepressed.

3-Iodo-naringenin-7 : 4′-dimethyl ether (IV a)

Naringenin-dimethyl ether (0·6 g.) was subjected to iodine treatment using the above procedure when it yielded the 3-iodo-derivative (0·6 g.), m.p. 164–66°, which agreed in melting point and colour reactions with the compound obtained by Goel *et al.*[1]

Action of alcoholic potash

It (0·6 g.) was treated with alcoholic potash (15 c.c.; 4%) for ten mitnues. The solution was acidified and the solid that separated was filtered and crystallised from alcohol to yield almost colourless needles of apigenin-7 : 4′- dimethyl ether, m.p. 170–71°.

3-Iodo-hesperetin-dimethyl ether (IV b)

Hesperetin-dimethyl ether (1 g.) dissolved in absolute alcohol (80 c.c.) was treated with silver acetate (2 g.) and iodine (0·85 g. in 20 c.c.) as in the case of O-dimethyl-naringenin. The 3-iodo-compound was crystallised from ethyl acetate petroleum ether mixture to yield pale yellow crystals (1 g.),

m.p. 155–56°. It gave a violet colour with alcoholic ferric chloride (Found: C, 47·8%; H, 4·0%; $C_{18}H_{18}O_6I$ requires C, 47·3%; H, 3·9%).

(*a*) *Action of alcoholic potash.*—The above compound (0·2 g.) after refluxing with alcoholic potash (25 c.c., 4%) for ten minutes was acidified and the solid obtained was crystallised from ethanol yielding luteolin trimethyl ether, as pale yellow needles, m.p. 160–61°.

(*b*) *Action of pyridine.*—3-Iodo-hesperetin-dimethyl ether (0·1 g.) was treated with pyridine (10 c.c.) and the solution heated over a boiling water-bath for two hours. The reaction mixture was poured into water (50 c.c.), the solid that separated was washed with dilute hydrochloric acid and subsequently with cold water. On crystallisation from ethanol it yielded luteolin-trimethyl ether (50 mg.), m.p. 160–61°.

3-Iodo-5: 7-dimethoxy flavanone (*III b*)

5: 7-Dimethoxy-flavanone (1·0 g.) was subjected to iodine oxidation as in the above cases. The 3-iodo-compound thus obtained separated from alcohol as colourless needles (0·8 g.), m.p. 183–84°.[1]

(*a*) *Treatment with alcoholic potash*

3-Iodo-5: 7-dimethoxy flavanone (1 g.) was heated with alcoholic potash (20 c.c., 4%) for ten minutes on a boiling water-bath. The alcohol was removed under reduced pressure; the solution was diluted, acidified and extracted with ether. The ether solution was washed successively with 0·5% and 10% sodium hydroxide solutions.

(i) 0·5% *Sodium hydroxide soluble fraction.*—The solution on acidification yielded a yellow solid (100 mg.) which on crystallisation from aqueous alcohol yielded yellow prisms, m.p. 178–80°, alone or mixed with galangin 5: 7-dimethyl ether (VI *a*), synthesised earlier by Kostanecki and Tambor.[5] It gave a reddish brown colour with alcoholic ferric chloride.

Its acetate prepared by heating it with acetic anhydride and pyridine crystallised from alcohol to yield colourless stout rectangular prisms melting at 184–86°. It agreed with the description of 3-acetoxy-5: 7-dimethoxy flavone.[5]

(ii) 10% *Sodium hydroxide soluble fraction.*—On acidification of the alkaline solution a colourless solid was obtained (400 mg.) which crystallised from methanol, chloroform and light petroleum mixture to give colourless needles, m.p. 170–71°. It gave no colour with alcoholic ferric chloride and also with magnesium and hydrochloric acid. Its properties agreed with

those of 2-hydroxy-2-benzyl-4: 6-dimethoxy-coumaranone[6] (VII) and the mixed m.p. with a synthetic sample was undepressed.

The above compound (50 mg.) was treated with concentrated sulphuric acid (5 c.c.) at 0° C. and the temperature was raised to 20° during half an hour. It was then poured into water when 4: 6-dimethoxy-benzal coumaranone, m.p. 151–52°, was obtained.

(iii) The ether solution which was freed from alkali-soluble fractions gave on evaporation chrysin-dimethyl ether (100 mg.), m.p. 115–17°.

(*b*) *Action with pyridine.*—The above iodo-compound (III *b*) (0·4 g.) was heated with pyridine (40 c.c.) on a boiling water-bath for two hours and the reaction mixture poured in water (100 c.c.). The solid that separated was washed with dilute hydrochloric acid and crystallised from ethanol to yield pale yellow plates of chrysin-dimethyl ether, m.p. 115–17°.

Iodine oxidation of hesperetin-dimethyl ether (*II b*)

Hesperetin-dimethyl ether (0·2 g.) was dissolved in glacial acetic acid (5 c.c.) and fused potassium acetate (0·5 g.) added. Iodine (0·2 g.) in glacial acetic acid (5 c.c.) was slowly added to the boiling mixture during one hour. The acetic acid was removed under reduced pressure and saturated sulphur dioxide solution (25 c.c.) added. The solid thus obtained was filtered, washed with cold water and dried in a vacuum desiccator. It was then repeatedly extracted with boiling ethyl acetate and the solution concentrated to about 15 c.c. To this was added petroleum ether (40–60°), when a yellow precipitate settled down. By controlled precipitation with petroleum ether all the yellow compound was precipitated. The solution was filtered (Filtrate F) and the yellow residue was crystallised from ethyl acetate yielding pale yellow crystals (40 mg.), m.p. 155–56°, undepressed when mixed with a sample of 3-iodo-hesperetin-dimethyl ether described already. On heating the above sample of iodo-compound with pyridine (2 c.c.) on a boiling water-bath for two hours and working up as mentioned above it gave luteolin-trimethyl ether, m.p. 160–61°. It contained no iodine and had R_f (circular) 0·82 in acetic acid water (3: 2) at 23°, the same as given by an authentic sample of luteolin 7: 3′: 4′-trimethyl ether.

The filtrate (F) was evaporated when a colourless solid (50 mg.), m.p. 160–61°, identical in colour reactions and m.p. with luteolin-trimethyl ether was obtained.

SUMMARY

A modified procedure for the action of iodine and silver acetate gives rise to purer products. Agreeing with earlier observations, hesperetin gives a good yield of 3-acetoxy hesperetin and hesperetin 7 : 3′-dimethyl ether yields the 3-iodo-compound. The iodoflavanones invariably yield the corresponding flavones by the action of pyridine. In the treatment with alcoholic potash, those which have a free 5-hydroxyl, *e.g.*, 3-iodo naringenin 7:4′-dimethyl ether and 3-iodo hesperetin 7 : 3′-dimethyl ether yield only the corresponding flavones; whereas 3-iodo-5 : 7-dimethoxy flavanone having no free 5-hydroxyl group gives a mixture of products, containing the flavone, the flavonol and the 2-hydroxy-2-benzyl 4 : 6-dimethoxy coumaranone. The difference seems to depend on the stability of the oxygen ring.

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NEW SYNTHESIS OF TAMARAXETIN, ALPINONE AND IZALPININ

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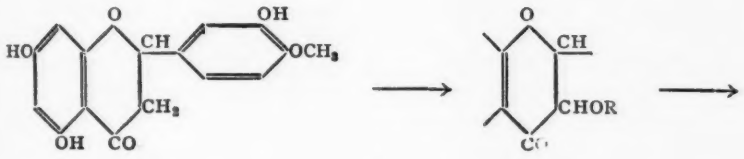
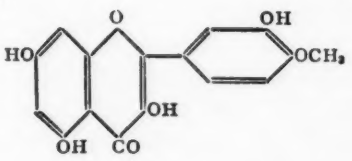
New methods of synthesis have been developed recently for the preparation of 3-hydroxy flavanones and since these compounds can be readily converted into the corresponding flavonols, they eventually provide more convenient methods of preparing naturally occurring flavonols also. As a typical example could be taken the synthesis of tamaraxetin (I) which is the 4′-mono-methyl ether of quercetin. Its earlier synthesis by Gupta and Seshadri,[1] using the well established method of Allan and Robinson, is rather tedious involving a number of steps. The alternative route now examined starts with hesperetin (II) which can be readily made from commercially available hesperidin.[2] Using iodine and silver acetate,[3] it can be conveniently converted into 3-acetoxy-hesperetin (III) which on subsequent hydrolysis gives 3-hydroxy-hesperetin (IV) in good yields. Subsequent dehydrogenation with iodine and potassium acetate in glacial acetic acid yields the flavonol tamaraxetin (I).



II

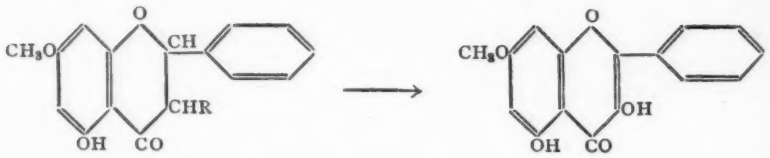
III, R=Ac.
IV, R=H.



I

The constitution of alpinone has been conclusively established[4,5] as 7-O-methyl pinobanksin (V). It is found to occur along with izalpinin (VI)

in the seeds of *Alpinia japonica*,[6] and these two are obviously related. It has been recently suggested[7] that the simpler flavanone structure represents an earlier stage in biogenesis and others involve further stages of oxidation. The feasibility of this scheme as a laboratory process has now been worked out. 5-Hydroxy-7-methoxy-flavanone (pinostrobin of pine heart-woods VII) which is conveniently obtained by partial demethylation[8] of the corresponding dimethoxy compound has been subjected to Fenton's oxidation[9] to yield alpinone (V). The alternative method used in the earlier case (iodine and silver acetate) is not suitable since, as is general with methyl ethers, here also the reaction stops with the stage of the 3-iodo-compound.[3] Alpinone (V) thus prepared could be dehydrogenated by iodine and potassium acetate to izalpinin (VI).



V. R=OH
VII, R=H

VI

EXPERIMENTAL

3-*Acetoxy-hesperetin* (*III*).—This was made earlier by Goel, Narasimhachari and Seshadri.[10] The modification of the general method recently described[3] gives better yields of the purer product. To hesperetin (1 g.) dissolved in absolute alcohol (30 c.c.) was added silver acetate (2 g.) and iodine (0·85 g.) in absolute alcohol (25 c.c.) at room temperature during a period of one hour with vigorous shaking. The mixture was then refluxed for two hours and the silver salt filtered off. Alcohol was then evaporated and the brown oily mass which solidified on cooling, was crystallised from ethyl acetate light petroleum mixture yielding aggregates of pale yellow tiny prisms (0·65 g.), m.p. 146–47°, agreeing with the m.p. given earlier by Goel, Narasimhachari and Seshadri.[11] It gave a violet colour with alcoholic ferric chloride.

3-*Hydroxy-hesperetin* (*IV*).—Earlier[10] the hydrolysis of the acetate was carried out by means of alkali; this has been found to give impure products owing to the formation of the corresponding benzyl coumaranone also. Hence acid hydrolysis has now been adopted. 3-Acetoxy-hesperetin (0·5 g.) was boiled with alcoholic hydrochloric acid (50 c.c., 1 : 1) for half an hour. Alcohol was removed under reduced pressure and ice added. The solid that separated was filtered, washed free of acid, dried in a vacuum desiccator

and crystallised from ethyl acetate light petroleum mixture yielding tiny prisms (0·3 g.), m.p. 200–201°, agreeing with the record of Zemplen and Bognar.[11] It gave a violet colour with alcoholic ferric chloride and was easily soluble in sodium carbonate. Its alcoholic solution gave a deep red colour with magnesium and hydrochloric acid and a pink colour with zinc and hydrochloric acid.

5:7:3′-*Trihydroxy*-4′-*methoxy flavonol* (*Tamaraxetin I*).—The above compound (0·2 g.) was dissolved in glacial acetic acid (6 c.c.) and fused potassium acetate (1 g.) added. The mixture was refluxed in an oil-bath and to the boiling solution iodine (0·16 g.) in glacial acetic acid (3 c.c.) was added dropwise during the course of an hour. The refluxing was continued for another hour, acetic acid removed under reduced pressure and sulphur dioxide water (50 c.c.) added to the residue. The solid thus obtained was filtered, washed with water and dried in a vacuum desiccator. It was first crystallised from ethyl acetate petroleum ether mixture and then from ethyl alcohol when tamaraxetin (0·12 g.) separated as golden yellow rectangular prisms, m.p. 260°, alone or mixed with an authentic sample earlier prepared by Gupta and Seshadri.[1]

Tamaraxetin tetra-acetate was prepared by the acetic anhydride pyridine method; it crystallised from alcohol as prismatic needles and rods, m.p. 203–04°.

3:5-*Dihydroxy*-7-*methoxy flavanone* (*Alpinone V*).—A suspension of finely powdered 5-hydroxy-7-methoxy flavanone (1 g.) in sulphuric acid (100 c.c., 2 N) was cooled in ice, vigorously stirred and hydrogen peroxide (5 vol., 80 c.c.) and ferrous sulphate solution (2%, 75 c.c.) were run in simultaneously during one hour. The mixture was allowed to stand for an hour and then extracted repeatedly with ether and the extract evaporated yielding a yellow solid. It was dissolved in alcohol (60 c.c.), a saturated solution of basic lead acetate (150 c.c.) added and the mixture allowed to stand overnight. A crystalline yellow lead salt separated (700 mg.) which was filtered, finely powdered and suspended in warm alcohol. Hydrogen sulphide was passed till the solution was saturated and the lead sulphide possibly containing some undecomposed lead salt was filtered off. This process was repeated twice again using the sulphide precipitate to ensure complete decomposition and complete recovery of the hydroxylated product. The total filtrate was evaporated to dryness when a pale yellow solid remained. It was first crystallised from ethyl acetate and light petroleum ether and then from methanol yielding colourless needles, m.p. 182–83°, agreeing with m.p. recorded earlier by Gripenberg[12] (Found: C, 67·1%; H, 4·8%;

$C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). It gave a reddish purple colour with alcoholic ferric chloride and a greenish indigo colour with conc. nitric acid. It developed a red colour with alcoholic magnesium and hydrochloric acid and a pink colour with zinc and hydrochloric acid.

3 : 5-*Dihydroxy-7-methoxy flavone* (*Izalpinin VI*).—To a solution of alpinone (V) (100 mg.) in glacial acetic acid (10 c.c.) was added fused potassium acetate (0·5 g.) and iodine (100 mg.) in glacial acetic acid (5 c.c.). The mixture was refluxed for 2 hours, acetic acid removed under reduced pressure and sulphur dioxide water added. The brownish yellow solid was filtered and dried in a vacuum desiccator. It was first purified by disolution in ethyl acetate and precipitation of the coloured impurities by controlled addition of light-petroleum and finally crystallised from alcohol yielding yellow needles (40 mg.), m.p. 195–96°. It agreed in its m.p. and colour reactions with izalpinin synthesised earlier by Rao and Seshadri.[13]

The diacetate of the above sample was prepared by the acetic anhydride-pyridine method; it crystallised from alcohol to give colourless needles, m.p. 172–73°. Rao and Seshadri[13] reported the same m.p. for izalpinin diacetate.

SUMMARY

A new and convenient method for the synthesis of tamaraxetin uses hesperetin. By the action of iodine and silver acetate, it is converted into 3-acetoxy-hesperetin and eventually into 3-hydroxy-hesperetin which undergoes dehydrogenation by means of iodine and potassium acetate to yield tamaraxetin.

5-Hydroxy-7-methoxy-flavanone (pinostrobin) is converted into alpinone by Fenton's oxidation and subsequent dehydrogenation yields izalpinin.

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EMISSION SPECTRUM OF BROMINE EXCITED IN THE PRESENCE OF ARGON

Part III. The Band System in the Region 2660-2590 Å

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Abstract

The wavelengths and wavenumbers of the band heads of the system 2660–2590 Å as obtained from the plates taken on the first order 21-feet grating spectrograph are given along with its vibrational analysis. This system is shown as the transition from an upper state at $T_e = 56776$ cm.$^{-1}$ with $\omega_e = 108{\cdot}0$ cm.$^{-1}$ to the $^3\Pi_u (O_u^+)$ state at $T_e = 15918$ cm.$^{-1}$ The lower state is the same as that of the two systems in the regions 2950–2670 Å and 3150–2970 Å reported earlier.

Introduction

In the earlier two papers[1,2] the band systems in the regions 3150–2970 Å and 2950–2670 Å were analysed and discussed. In this paper the band system in the region 2660–2590 Å will be analysed and discussed.

Vibrational Analysis

The experimental details are the same as described in the earlier paper.[1] The wavelengths and wavenumbers of the band heads of the system 2660–2590 Å measured from the plates taken on the 21-feet grating spectrograph in the first order are given in Table I. This system is very weak and the band heads are not sharp. Therefore the error involved in the measurements of band heads may be upto $\pm$ 5 cm.$^{-1}$ The vibrational analysis and the corresponding intensity distribution and Frank-Condon parabola are given in Tables II and III respectively.

The vibrational analysis shows that the lower state of the system is the upper state of the visible absorption band system in the region 8672–5110 Å.

* Now Senior Research Fellow of the Council of Scientific and Industrial Research, Govt. of India.

TABLE I

Wavelengths, wavenumbers and relative intensities of the bands in the 2660–2590 Å system

I	λ_{air}	ν_{vac}	I	λ_{air}	ν_{vac}
2	2663·0	37541	1	2631·8	37986
3	59·2	594	1	29·3	38022
1	55·7	644	2	28·0	040
1	54·9	655	0	26·6	061
3	52·1	695	1	24·9	085
2	50·9	712	2	22·1	126
3	48·8	741	2	19·8	160
3	47·5	760	2	17·0	200
2	46·6	773	2	15·2	227
5	45·3	792	1	12·6	265
2	43·7	815	1	10·3	298
2	42·1	837	1	07·2	344
7	40·5	860	0	05·2	373
0	39·4	876	2	03·9	392
3	38·5	889	2	01·9	422
1	36·8	913	2	00·6	441
3	34·1	952	1	2598·0	480

This state, as shown in the earlier two papers,[1,2] is also the lower state for the system 2950–2670 Å as well as for the 3150–2970 Å. The $\triangle G'(v+\frac{1}{2})$ and $\triangle G''(v+\frac{1}{2})$ values for the system are shown in Table II. The $\triangle G''(v+\frac{1}{2})$ values for the lower state as obtained by Venkateswarlu and Verma[1] from the analysis of the 2950–2670 Å system along with those obtained by Darbyshire[3] and Brown[4] from the analysis of the visible absorption bands are also included in Table II for comparison.

The observed $\triangle G'(v+\frac{1}{2})$ values could be fairly well represented with the vibrational constants $\omega_0 = 106{\cdot}5\ \text{cm.}^{-1}$ and $\omega_0 x_0 = 1{\cdot}5\ \text{cm.}^{-1}$ The vibrational constants for the lower state are those obtained by Darbyshire[3] from the analysis of the visible absorption band system.

It is to be mentioned that no reliable isotopic shifts could be measured though one expects two weak isotopic band heads for each main band. This

TABLE II

The vibrational analysis of the system 2660–2590 Å of bromine molecule

v'' / v'	21	22	23	24	25	26	27	28	29	30	31	32	$\Delta G'(v+\frac{1}{2})$ Obs.	$\Delta G'(v+\frac{1}{2})$ Cal.
0					37913	37837	37773	37712	37655	37594	37541			
					76	64	61	57	61	53				
					109	115	103	103	105	101	103		105·6	105·0
1					38022	37952	37876	37815	37760	37695	37644			
					70	76	61	55	65	51				
					104	109			100	97	97		101·4	102·0
2	38422	38344	38265	38200	38126	38061			37860	37792	37741	37695		
	78	79	65	74	65				68	51	46			
		97	108	98	101	99				97	96	97	99·1	99·0
3		38441	38373	38298	38227	38160				37889	37837	37792		
		68	75	71	67					52	45			
				94						97			96·5	96·0
4				38392					38040	37986				
									54					
				88						99			93·5	93·0
5				38480						38085				
$\Delta G''(v+\frac{1}{2})$ Obs.		78·0	73·5	70·0	72·5	69·5	70·0	61·0	56·0	62·0	51·8	45·5		
$\Delta G''(v+\frac{1}{2})$ P.V. & R.D.V.		89·0	87·0	76·4	73·5	72·0	69·0	62·6	55·3	51·5				
$\Delta G''(v+\frac{1}{2})$ O.D. & W.G.B.		81·9	80·0	76·1	71·0	67·3	65·6	61·3	55·5	49·1				

TABLE III

Intensity distribution and Frank-Condon parabola for the bands in the system λ 2660–2590 Å

v″ / v′	21	22	23	24	25	26	27	28	29	30	31	32	33
0					1	2	2	2	1	3	2		
1					1	3	0	2	3	3	1		
2	2	1	1	2	2	0			7	5	3	3	
3		2	1	1	2	2				3	2	5	
4				2					2	1			
5				1						1			

is probably because the system is extremely weak and superposed by the extensive continuum mentioned in the first paper (Part I).[1]

THE ELECTRONIC TRANSITION INVOLVED

The lower state of the system according to the analysis given is the well known $\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u$ $^3\Pi_u (O_u^+)$ state at $T_e = 15918$ cm.$^{-1}$ The electronic state involved for the upper state lies at $T_e = 56776$ cm.$^{-1}$ The electronic states $^1\Sigma_g^+ (O_g^+)$ and $^3\Sigma_g^- (O_g^+ \text{ or } 1_g)$ arising from the configuration $\sigma_g^2 \pi_u^2 \pi_g^4 \sigma_u^2$ were attributed earlier[1, 2] tentatively to the states at 51802 and 48516 cm.$^{-1}$ respectively which forms the upper states of the 2950–2670 Å and 3150–2970 Å systems. The next higher configuration[5] giving *gerade* states is $\sigma_g \pi_u^4 \pi_g^3 \sigma_u^2$ which gives $^1\Pi_g (1_g)$ and $^3\Pi_g (2_g, 1_g, O_g^+)$ states. Venkateswarlu[6] attributed tentatively $^1\Pi_g (1_g)$ to a level at 61444 cm.$^{-1}$ with $\omega \sim 220$ cm.$^{-1}$ which gives rise to groups of diffuse emission bands without the presence of argon. He attributed $^3\Pi_g (1_g)$ to a level at 55534 cm.$^{-1}$ with $\omega \sim 330$ cm.$^{-1}$ which also gives rise to groups of diffuse emission bands in the absence of argon. There is a possibility that the upper level of the present system is $^3\Pi_g (O_g^+)$, but one wonders why the frequency for this state is only 108·0 cm.$^{-1}$ while it is so much higher for $^3\Pi_g (1_g)$ and $^1\Pi_g (1_g)$ arising from the same configuration. This difference in the ω values can, however, be understood on the basis that these levels may have different dissociation products and dissociation

limits. On the other hand, since the band system 2660–2590 Å is extremely weak, it is also possible that it may be due to a forbidden transition in which case the upper state may be $\sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^2\ {}^1\Delta_g\ (2_g)$ or $\sigma_g\ \pi_u{}^4\pi_g{}^3\ \sigma_u{}^2\ {}^3\Pi_g(O_g^-)$. Because of these different possibilities it is not easy to choose a particular electronic term for the upper level of the 2660–2590 Å system.

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